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Part II.

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16. ABSTRACT

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IMPROVEMENT AND EVALUATION OF METHODS FOR SULFATE ANALYSIS
PART II

Final Report

by

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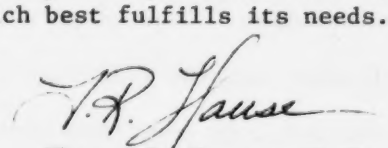
FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

The work covered in this report details efforts performed for the Environmental Monitoring Systems Laboratory to improve methodology used to monitor air pollution concentrations. Several procedures for analyzing the sulfate content of ambient aerosols collected on various filter types were evaluated for precision, accuracy, working range, and intermethod comparability. The work reported here and in phase I of this project (EPA-600/4-79-028, April, 1979) should provide air pollution agencies with information about the reliability of several different sulfate analytical procedures and help each agency choose the analytical procedure which best fulfills its needs.



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ABSTRACT

Methods for extraction of sulfate from glass fiber hi-vol and Teflon lo-vol samples were evaluated. Efficiencies were found to vary with sampling location up to 20%. Mechanical shaking in water at room temperature was significantly more efficient than ultrasonic or reflux techniques with hi-vol samples. While Teflon filters are not wet by water, pre-wetting of filters with methanol did not significantly enhance sulfate extraction. A turbidimetric sulfate method using SulfaVer IV was evaluated for ruggedness, precision and intermethod agreement. Its precision was at least equal to that of a conventional turbidimetric method but its accuracy was somewhat less, especially at lower sulfate levels. The Dionex Model 10 ion chromatograph was evaluated for low level sulfate analysis using both a sample pre-concentrator and large (0.5 ml) sample loop. The latter was the preferred technique for samples $\leq$ 20 µg/ml. Accuracy was within 15% in the range 2 to 20 µg/ml with a median C.V. of 6.5% for 24 atmospheric samples. This range will permit sulfate analysis of 24 hour fine particulate samples collected with dichotomous samplers. Use of a sample pre-concentrator permitted analysis of samples containing < 1 µg/ml sulfate.

This work is submitted in fulfillment of Grant No. 805-447-1 by the California Department of Health Services under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period October 1, 1978 to Sept. 30, 1979, and work was completed as of May 27, 1979.

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Mr. J. C. Puzak served as Project Officer for this program. His helpfulness throughout this work has been sincerely appreciated.

I. INTRODUCTION

In preceding EPA-sponsored programs, a series of wet chemical sulfate methods was evaluated and compared to one another and in some cases, to total sulfur determinations by x-ray fluorescence analysis.[1-3] These methods were:

--Barium sulfate turbidimetric procedures (Public Health Service,[4] AIHL Method 61 and an improved version, AIHL Method 75),

--A barium sulfate turbidimetric method using SulfaVer IV^{R},

--Automated methylthymol blue procedures (Midwest Research Institute,[5] the Colovos[6] and AIHL versions),

--The AIHL microchemical method,[7]

--Two modifications of the thorin method as developed by C. Brosset,[8]

--A manual barium chloranilate method,[9]

--The Dionex ion chromatograph.[10]

Typically, the methods were evaluated for precision, accuracy, working range, interference effects and comparability of results with atmospheric samples. In one case a ruggedness test was performed.

The current program includes work done in the period October 1978-March 1979 to complete EPA Grant No. 805-447-1. It continues sulfate studies including (1) an evaluation of sulfate extraction procedures

for glass fiber hi-volume filter and Teflon low-volume filter samples, (2) a determination of the shelf-life of the pre-mixed reagent used in barium sulfate turbidimetric AIHL methods 61 and 75, (3) a ruggedness test and optimization of a turbidimetric procedure using SulfaVer IV^{R},[11] (4) an evaluation of the Dionex ion chromatograph for sulfate analysis of extracts from low-volume filter samples such as anticipated with a dichotomous sampler network and (5) an intermethod comparison with the methods evaluated.

II. SUMMARY AND CONCLUSIONS

Evaluation of procedures for aqueous extraction of sulfate from glass fiber hi-vol filter samples has demonstrated that 30 minutes ultrasonic extraction and 60 minute reflux procedures are not significantly different. However, these techniques give sulfate recoveries 2-3% lower than mechanical shaking for 60 minutes at room temperature. Ultrasonic extraction for 5 minutes is substantially poorer in efficiency. Systematic variation in sulfate recoveries with sampling location was observed.

Using Berkeley low-volume atmospheric samples on Teflon membrane filters, four sulfate extraction techniques gave results which were equal within experimental error. However, with samples collected adjacent to a Los Angeles freeway, heating in hot water at 80°C in sealed tubes was notably less efficient than 30 minutes ultrasonic extraction with or without pre-wetting with methanol, or mechanical shaking for 60 minutes. The latter averaged about 90%. The use of methanol to pre-wet the filters did not cause a consistent improvement in extraction efficiency and is not recommended. The choice between mechanical shaking and ultrasonic extraction can probably be based on convenience and personnel costs. It remains unclear what effect, if any, simultaneous ultrasonic extraction of large numbers (> 8) samples has on extraction efficiency. Similarly the effect of position within the bath, in relation to standing waves set up by ultrasonic vibration, was not evaluated. Finally, the need exists to obtain a quantitative measure of ultrasonic energy output. Lacking such a measure the generality of the current study, which used a Bransonic Model 42 150 watt input ultrasonic bath, remains unclear.

Sulfate was substantially more difficult to extract from the freeway particulate enriched samples. This may relate to the presence of oily particulates, or, and less likely, relatively insoluble sulfates (e.g. lead sulfate). The former hypothesis would be consistent with results with the hi-vol filter samples.

A pre-mixed reagent for stabilizing suspensions of barium sulfate in turbidimetric sulfate analysis (AIHL Methods 61 and 75) was shown to have a shelf life of more than 15 months.

A turbidimetric sulfate method utilizing SulfaVer IV^{R} was subjected to an 11 parameter ruggedness test. Choice of sulfate level at 300 or 1300 µg/20 ml was the dominant source of variance in the method; at the lower sulfate level results were substantially in error. The optimized procedure (Appendix G) utilizes reagent-sample mixing as well as absorbance readings in one inch diameter, sealed test tubes to eliminate sample transfers.

The Dionex Model 10 ion chromatograph was evaluated for use in analyzing low level (< 20 µg/ml) sulfate samples such as obtained from dichotomous samplers. Both a large sample loop and a sample pre-concentrator were evaluated for this application. The latter was found especially useful for samples < 1 µg/ml and showed excellent linearity and accuracy with standards. However, for routine analysis, an 0.5 ml sample loop provided a simpler procedure and an adequate analytical range. Accuracy with the 0.5 ml sample loop was hampered, however, by non-linearity of the working curve below about 5 µg/ml. Nevertheless, the method remained accurate within 15% in the range 2 to 20 µg/ml, as measured with EPA

sulfate audit strips. Precision, as expressed by C.V. values, was $\leq$ 5%. Nitrate was shown to provide insignificant interference, even with the use of a 250 mm anion separator column, if the trailing peak height method was used.

An intermethod comparison was done for the SulfaVer IV^R method using 24 hi-vol extracts. It was compared to an automated methylthymol blue (MTB) procedure with results for the latter being calculated with and without correction for initial sample absorbance. The SulfaVer IV^R method was, on average, 10% higher than the corrected MTB results and 4% higher than the uncorrected MTB results. The median C.V. for 24 samples, analyzed with three determinations on separate days, was 3.2%. This is somewhat better precision than previously found with this method or with Method 61 and 75 probably as a result of the use of a better quality spectrophotometer and the elimination of sample transfers. The accuracy of the method is somewhat poorer compared to conventional turbidimetric sulfate methods using barium chloride.

An intermethod comparison was done between the Dionex IC, MTB (0-10 µg/ml range) and AIHL microchemical methods. On average, IC results were lower than those by the MTB procedure by 7%, but agreed within 2% with those by the AIHL micro method. The median C.V. for the IC method was 6.5%.

Based on evaluations of accuracy, precision and intermethod comparison the SulfaVer IV^R procedure, AIHL Method 79, can be employed as an alternative to conventional turbidimetric sulfate analysis in 24 hour hi-volume filter samples. Similarly, the Dionex ion chromatograph with 0.5 ml sample loop can be used for analysis of sulfate in the range

$\leq$ 20 µg/ml such as can be obtained with extracts from 24 hour dichotomous filter samples. However, the non-linearity of the working curve observed below 5 µg/ml decreases accuracy unless additional standards are employed. For samples < 1 µg/ml, a sample pre-concentrator is necessary.

III. SULFATE EXTRACTION EFFICIENCY STUDIES WITH GLASS FIBER HI-VOL FILTER SAMPLES

A. Introduction

At least three procedures are in use by monitoring organizations for the extraction of water soluble ions from atmospheric samples. These include 30-minute ultrasonic extraction at room temperature,[5] 60-minute heating under reflux,[12] and 60-minute mechanical shaking in water at room temperature.[13] The aims of the present study were 1) to compare these procedures, and 2) to determine their absolute efficiencies for removal of water soluble sulfate. The specific procedures evaluated were as follows:

1. Ultrasonic extraction in 50 ml H_2O as in Reference 12 but for 5 minutes and using 60 ml Erlenmeyer flasks with ground glass stoppers.

2. As in (1) but for 30 minutes (the time specified in Reference 12).

3. 60 minutes boiling under reflux as in Reference 13 which includes filter rinsing. Final volume 100 ml.

4. Mechanical shaking with a Burrell wrist action shaker in 50 ml H_2O at room temperature contained in 250 ml flasks sealed with Parafilm.[13]

Detailed protocols for the procedures followed are included as appendices A-C.

In all cases extraction was followed by filtration through an 0.7 µm pore size cellulose ester Millipore filter using a Millipore filtration apparatus. Only with the reflux procedure were the glass fiber and Millipore filters rinsed following filtration. As a result this study represents a comparison of the extraction process, itself, minimizing variations introduced by subsequent sample handling.

After comparing sulfate recoveries by the four methods, the efficiency of each method for extraction of sulfate was established by determining the amount of sulfate remaining unextracted following initial extraction with one of the four methods. The approach used was to repeatedly re-extract the filter residue and analyze these extracts for sulfate. By choosing the reflux procedure for this purpose the problem of sulfate in the extract remaining wetting the filter was minimized since in this procedure, the filter is rinsed with water. Following the initial extraction by refluxing, the residual filter was re-extracted by the reflux method using 35 ml H_2O and, with washings, brought to 50 ml for analysis. The residue from this extraction was extracted a third time in 15 ml water by 30 minutes ultrasonic extraction. The sum of the sulfate recovered on the quarters by successive extractions was taken as the total water soluble sulfate. Efficiencies for each extraction method were calculated relative to these totals. Thus, only the efficiency for extracting water soluble sulfate is being measured. Insoluble sulfates, if present, are not considered. (Past studies comparing x-ray fluorescence analyses for sulfur to water extractable sulfate have failed to establish a significant difference. Accordingly, the distinction between "total sulfate" and "total water soluble sulfate" might be academic).

B. Preliminary Evaluation to Establish Variability Between Filter Quarters

The experimental procedure requires sectioning a set of 8 x 10" hi-vol filter samples into quarters and extracting each of the four quarters from a given filter by one of the four methods. The ability to discern differences between extraction methods is limited by the inherent variability between the quarters of a given filter and the precision of the analytical method. To measure this variability, four hi-vol filters were quartered and the 16 quarters extracted by the 30-minute ultrasonic extraction procedure. For this trial the filter quarters included the usual two borders without particulate. Since filters are rarely mounted in such a way as to yield equal borders on all sides, effort was made to quarter the filters to provide equal loaded areas. However, because the sealing gasket on the sampler is not a perfect rectangle (it is typically curved slightly into arcs) the quarters could not be conveniently cut into identically loaded area. This would contribute to any variability observed.

The extracts were analyzed by an automated MTB method as solutions in the range 16 to 61 µg/ml sulfate.* The analytical protocol has been described and evaluated previously.[2] A check of accuracy and precision of the method using EPA audit strips to provide solutions in this range is given in Table 1, and was made as part of the current study. Results indicate that the differences between the theoretical and recovered sulfate for the MTB method are 3% or less and the coefficient of variation for four strips at each level, is in the range 0.5 to 4.9% increasing with decreasing sulfate concentrations.

*Analyses were done in the range 0-100 µg/ml using MTB levels uncorrected for impurities and a third order regression fit to the resulting non-linear working curve.

Table 1

Accuracy and Precision of the
MTB Method Using EPA Audit Strips

Sample	Theoretical Value (µg/strip)	(µg/ml)	Obs.[a]/Theoret.	C.V.
9000 Series	745.6	14.9	1.00	4.9
712-5000 Series	2250	45.0	0.98	0.5
712-6000 Series	2700	54.0	0.97	1.8

a. Mean results for four strips extracted by 30-minute ultrasonic extraction, calculated using third order regression data analysis.

The results of the quarter filter variability study are given in Table 2 expressed as μg sulfate per quarter. The results indicate a coefficient of variation ranging from 1 to 10%, again, increasing with decreasing sulfate loading. If variation in loaded filter area were the dominant source of variability it would be expected that the C.V. would be invariant with loading in contrast to the results obtained. Since quarters were cut to equalize loaded areas rather than filter surface, some variation in the sulfate contributed by the blank filter would be expected. However, the mean sulfate blanks for all batches of EPA Grade* glass fiber filters are < 0.7 $\mu g/cm^2$ suggesting negligible contribution to the variability observed. We conclude therefore, that, except for the most lightly loaded sample, the observed variability reflects principally the variability of the analytical method. For the exception, variability in sulfate loading and/or loaded filter area contributes roughly equally.

To minimize observed variability between quarters for extraction method comparisons, the 24 filter samples used were restricted to those from sites within California's South Coast Air Basin likely to exhibit relatively high sulfate levels. As a result, the minimum sulfate per quarter proved to be about 1700 μg. To further reduce variability the borders from all filters were removed before quartering leaving a rectangle containing only loaded filter area. This was then quartered to provide four quarters equivalent in an area (about 98 cm^2) within an estimated 1%. Based on the above and results for sample 4, Table 2, the variability between quarters

*This is the manufacturer's designation and does not imply approval by the U.S. Environmental Protection Agency.

Table 2

Determination of Variability Between
Quarters Cut from 8 x 10" Hi-Vol Filters

Sample	Sulfate Analyzed (µg/ml)	Mean Sulfate Per Quarter (µg)	C.V.[a] (%)
1	16.4	821 ± 86	10.4
2	25.8	1288 ± 73	5.6
3	25.9	1294 ± 66	5.1
4	60.7	3034 ± 36	1.2

a. The C.V. vs. sulfate loading relationship is approximately linear in a log-log plot.

from one filter extracted by one method and analyzed by the MTB procedure, is estimated to be about 1% (C.V.).

Following re-extractions, extracts were analyzed by the AIHL microchemical method,[7] Since > 85% of sulfate was removed by the initial extraction, the variability in the microchemical method for analysis in the range 0.7 to 5 µg/ml (≤ ca. 15% C.V.), as obtained on extracts from the first re-extraction, has reduced significance.

C. Results

Results for the sulfate recovered from each quarter by each procedure are given in Table 3. Inspection of individual as well as the mean recovered sulfate values suggests that 5 minutes ultrasonic extraction is clearly less efficient than the other procedures while 30 minutes ultrasonic and the 60-minute reflux procedures yield very similar results. The mechanical shaking procedure recovers on average, about 3% more sulfate compared to 60-minute reflux. A "t" test of paired differences reveals this difference to be significant at nearly the 99% confidence level (t = for 23 degrees of freedom 2.786).

Results for re-extraction following 60 minutes reflux indicates about 2% additional sulfate can be recovered by a second reflux. Results from a second re-extraction were below detection. A t-test of paired differences between results by 60-minute mechanical shaking and the total water-soluble sulfate (i.e. the sum of the sulfate recovered by 60-minute reflux and the first re-extraction) indicated these were not significantly different.

Table 3

Recovery of Sulfate from Extraction of Quarters from 8 x 10" Glass Fiber Filter ($\mu g\ SO_4^{=}$)[a,d]

Site	Filter	5 Min Ultrasonic	30 Min Ultrasonic	60 Min Reflux	60 Min Shaking	Re-extraction After 60-Minute Reflux First[b]	Re-extraction After 60-Minute Reflux Second[c]
Anaheim	1	2600	3030	2950	3020 2920	73.7	< 7.5
	2	2340	2690	2970	2920	39.2	< 7.5
	3	2760	3190	3260	3440	72.0	< 7.5
	4	3440 3350	3550	3740	3780	60.6	< 7.5
	5	3410	3650	3860	3830	118	< 7.5
Long Beach	1	4800	5000	5990	5750 5600	106	< 7.5
	2	10500	11400	12200	12300	302	< 7.5
	3	5890	6540 6520 6690	6640	6300 6430	122	< 7.5
Downtown Los Angeles	1	4320	4910	5070	5170	69.7	< 7.5
	2	2960	3280 3200	3040	3240	70.1	< 7.5
	3	2880	3130	3190	3320	55.8	< 7.5
	4	2110	2370	2480	2700	49.1	< 7.5
	5	7120	8070	8230	8670	158	< 7.5
	6	4140	4780	4670	4490	73.6	< 7.5
Pasadena	1	6500	8070	7280	7690	121	< 7.5
	2	1400	1680	1780	1740	71.8	< 7.5
	3	4070 4030	4720	4410	5350 4810	77.1	< 7.5
Santa Ana	1	1910	2080	2160	2240	34.3	< 7.5
	2	2560	2800	2820	2980	72.3	< 7.5
	3	2760	3450	3190	3440	66.3	< 7.5
	4	5280	5700	5790	5810	142	< 7.5
	5	2290	3200	2720	3100	69.4	< 7.5
	6	3670	4170	4120	4320	143	< 7.5
	7	2970	3330 3400	3200	3540	254	< 7.5
Mean:		3859	4368	4407	4533	101	---

a. Filters are 24-hour hi-vol samples obtained with EPA Grade filters from J. Wendt, CARB.
b. By 60-minute reflux method but with final volume 50 ml.
c. By 30-minute ultrasonic extraction method but in 15 ml H_2O.
d. Multiple values for a given sample indicate replicate analyses.

Based on mean recovered sulfate levels, the average efficiency of each procedure for extraction of water soluble sulfate from 24-hour hi-vol glass fiber filter samples is given in Table 4.

The high sulfate recovery by the 60-minute mechanical shaking method prompted further data evaluation to determine if this efficiency might be subject to variation with sample type as implied by differences in sampling location. Mean recoveries of sulfate, expressed as percents of the total water-soluble sulfate, are given in Table 5. Data have been arranged to list sites by increasing distance from Long Beach. Since in some cases only 3 or 5 samples were obtained at a given site, no firm conclusions may be made. However, the data suggest that with samples obtained at increasing distance from Long Beach, mechanical shaking in cold water becomes relatively more efficient. Since the Long Beach area is one especially rich in hydrocarbons because of oil fields and refineries, aerosols may be especially oily and difficult to wet by aqueous extraction. This offers at least a simplistic rational for these observations. Further studies would be needed to confirm the validity of this site-specificity.

We conclude from these studies that the 30-minute ultrasonic and 60-minute reflux procedures are not significantly different in efficiency. Except for relatively unusual sampling locations, the mechanical shaking procedure usually provides the highest sulfate recovery. Since this method offers decided advantages in simplicity and reduced equipment cost compared, at least, to the reflux method, consideration of its wider use should be given.

Table 4

Average Efficiencies for Extraction of Water Soluble Sulfate from 24-hour Hi-vol Glass Fiber Filter Samples

Method	Efficiency (%)[a]
5 min. ultrasonic	85.6
30 min ultrasonic	96.9
60 min reflux	97.8
60 min shaking	100

a. Calculated relative to sulfate recovered by successive extractions by the reflux method.

Table 5

Mean Recoveries of Sulfate by 60-Minute Mechanical Shaking as a Function of Location

Site	Distance Inland from Pacific Coast at Long Beach, KM	N	Mean % Recovered[a]
Long Beach	0	3	96.0
Anaheim	22	5	98.8
Downtown Los Angeles	32	6	101.6
Santa Ana	32	7	102.6
Pasadena	42	3	105.6

a. Relative to the total water soluble sulfate determined by successive extractions by the reflux method.

Further work is needed to determine the significance of sulfate recoveries above 100% observed by this method with nearly 70% of the samples. One possible cause would be greater extraction of a negative interferent (e.g. Ba^{+2}) from the glass fiber filter at reflux compared to room temperature.

IV. SULFATE EXTRACTION EFFICIENCY STUDIES WITH TEFLON LO-VOL FILTER SAMPLES

A. Introduction

Previous AIHL studies[14] have evaluated procedures for the extraction of sulfate and nitrate from filter samples collected on 47 mm cellulose acetate membrane and glass fiber hi-vol filters. With the low-volume samples a micropercolation technique[15] was shown to be about 99% efficient for sulfate extraction. With glass fiber filters, sulfate extraction efficiency for micropercolation was 92%, equivalent to that by a simpler procedure, immersion of the sample in water at 80°C in sealed test tubes.

Aqueous extractions of sulfate from Teflon filter samples is more difficult, in relation to cellulose ester and glass fiber filter samples, because of its non-wettability in water and low density causing it to float. Stevens et al[16] reported use of ultrasonic extraction for 20 minutes with water at room temperature, the filter being held submerged and unfolded by a fluted Teflon pipe, the end resting on the unloaded edge of the filter. The samples were continuously moved within the bath because of concern about variability in agitation with bath location. By comparison with x-ray fluorescence analysis for sulfur, the efficiency for sulfate extraction was inferred to be 95-98%.

B. Experimental Procedure

The present study has emphasized aqueous extraction procedures potentially useful for processing large numbers of samples such as anticipated from the dichotomous sampler network. The procedures

evaluated were:

1. Mechanical shaking 60 minutes with an Eberbach platform shaker with samples in test tubes and filters cut into quarters (Appendix D).

2. Ultrasonic extraction for 30 minutes, with sample pre-wet with methanol and weighted down with a glass rod (Appendix E).

3. Same as 2 omitting methanol.

4. Heating at 80°C for two hours in sealed test tubes with filters cut into quarters (Appendix F).

The study employed two groups of 24 filters each. Group A included 24-hour samples collected without size segregation in Berkeley* approximately 27 m above street level using 47 mm Fluoropore filters mounted in an open face filter holder. Group B were 24-hour fine particulate samples collected on 37 mm Fluoropore filters using two dichotomous samplers. Samplers were located 8 meters east of the eastern edge of the San Diego Freeway, in West Los Angeles, about 2 meters above the roadway. Average traffic volume on this freeway is 250,000 cars/24 hours. By employing samples of diverse origin it was intended to provide differing matrices for sulfate extraction. Since higher sulfate levels were anticipated for the Los Angeles samples, and since sufficient extract for inter-method comparison was needed, the Los Angeles samples were extracted in 20 ml H_2O. Berkeley samples used 10 ml H_2O.

*Samplers at 2151 Berkeley Way, in downtown Berkeley.

Six samples from each of the two locations were extracted by each of the four extraction procedures. Following vacuum filtration the quantity of sulfate in the solution remaining wetting the particulate matter on the filter was determined by weighing the Teflon filters wet and after drying to constant weight at 105°C. With the weight difference and the sulfate concentration measured in the extract, the sulfate remaining in the aqueous phase on the filter was calculated. Sulfate in the extract was determined by an automated methylthymol blue (MTB) procedure and by the AIHL microsulfate method. The MTB procedure followed was that described in Reference 2 in which no effort is made to linearize the working curve by altering reagents but the working curve is fit by non-linear regression. By eliminating sample dilution the procedure was applied in the 0-10 µg/ml range. No correction for sample color was made. However, the resulting error is expected to be small relative to that with hi-vol samples (e.g. 6% error with samples described in Table 19, page 65). Calculation of extraction efficiency employed the mean results from the two procedures.

To determine the sulfate remaining unextracted after the first extraction, two filters were extracted together by the mechanical shaking procedure (1), but for 24 hours, in 5 ml H_2O. Filters were combined since it was considered likely that the sulfate in extracts from single filters would be too dilute for reliable analysis. Extracts from this second extraction were analyzed with the Dionex IC using a sample pre-concentrator.

The efficiency of the initial extraction by each method was calculated as follows:

$$\% \text{ Extraction Efficiency} = \frac{S_1}{S_1 + (S_2 - R)} \times 100$$

where S_1 = total micrograms of sulfate recovered by the initial extraction from extracting two filters separately.

S_2 = total micrograms of sulfate recovered in the second extraction of the two filters combined.

R = total calculated sulfate remaining in aqueous phase clinging to the two filters after initial extraction.

C. Results

The levels of sulfate recovered by the second extraction were relatively low, and, in principal, might reflect the influence of contamination or other artifacts. Accordingly, a relationship was sought between the sulfate recovered by the first and second extractions for filter pairs (Figure 1). The figure suggests a significant positive relationship between levels of sulfate recovered by successive extraction. Thus sample contamination or other artifacts do not appear to be influencing the level of sulfate recovered by the second extraction. The Los Angeles samples yielded substantially higher second extraction sulfate levels.

The extraction results are tabulated in Tables 6 and 7 for Berkeley and Los Angeles samples, respectively. In contrast to expectations

Figure 1

COMPARISON OF SULFATE RECOVERED BY SUCCESSIVE EXTRACTIONS OF FLUOROPORE FILTER SAMPLES

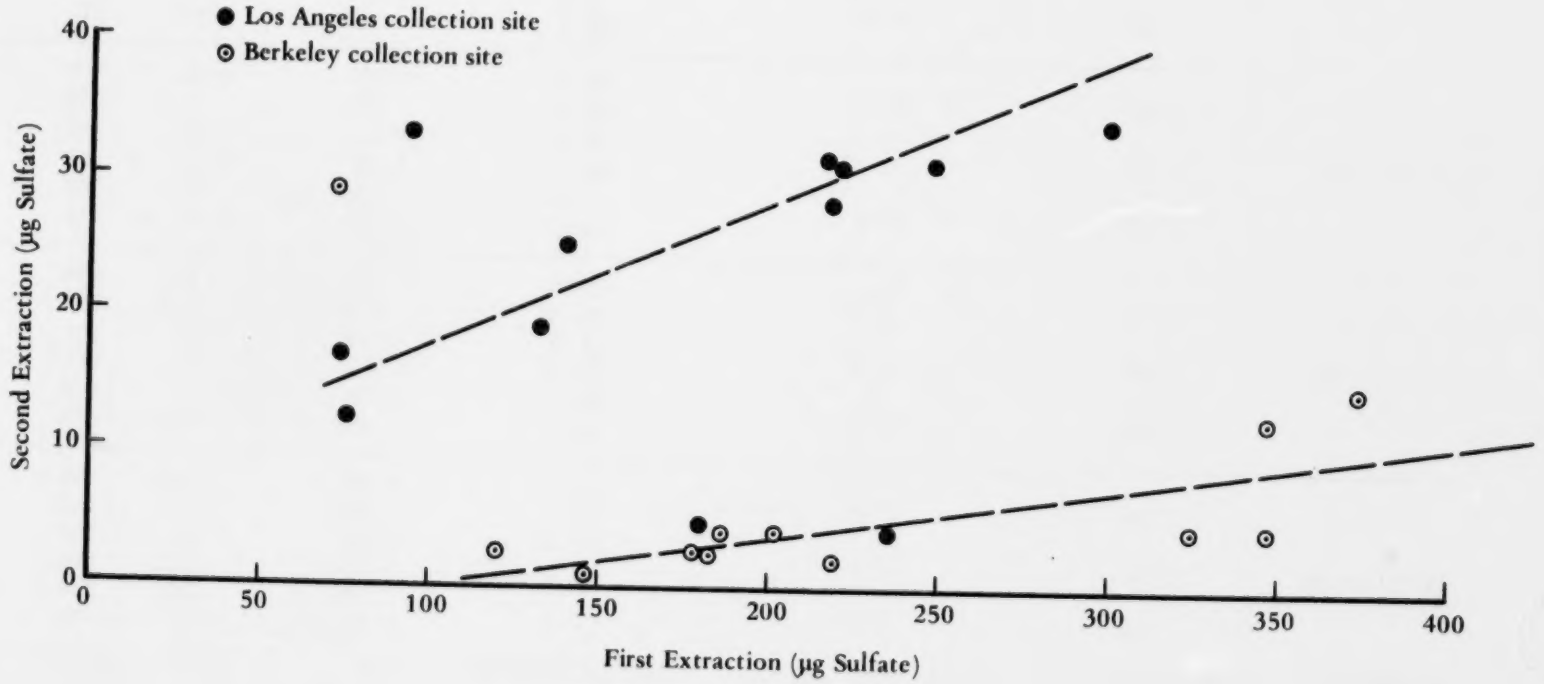

Table 6

Recovery of Sulfate and Efficiency of Extraction with Lo-Vol Teflon Filter Samples from Berkeley[a]

Method	Filter Code[d]	µg $SO_4^=$ from First Extraction AIHL	µg $SO_4^=$ from First Extraction MTB	µg $SO_4^=$ in Residual Extract Wetting Filter	µg $SO_4^=$ in Second Extract of Filter Pair by IC	Average Extraction Efficiency for Filter Pair[b]	Mean (C.V., %) Extraction Efficiency for Method
Mechanical Shaking	B1A	76.2	76.8	1.03	14.5	96.7	98.2 (1.3)
	B2A	290	304	0.74			
	B3A	250	266	0.94	4.25	99.1	
	B4A	82.4	96.5	0.22			
	B5A	101	108	0.54	4.15	98.7	
	B6A	101	94.4	1.04			
Ultrasonic with MeOH	B1B	145	145	0.82	2.35	99.2	98.6 (1.6)
	B2B	25.3	47.2	0.09			
	B3B	44.0	52.5	0.11	0.75	99.8	
	B4B	96.5	96.8	0.33			
	B5B	142	161	0.50	12.4	96.8	
	B6B	192	199	0.58			
Ultrasonic	B1C	79.9	81.8	0.71	2.10	100.0	99.9 (0.1)[d]
	B2C	131	145	0.73			
	B3C	28.9	34.9	0.08	29.0	(71.5)[c]	
	B4C	36.0	43.6	0.32			
	B5C	119	138	1.78	2.50	99.8	
	B6C	34.8	66.8	0.29			
Heating at 80°C	B1D	114	135	1.38	4.10	99.4	99.8 (0.4)
	B2D	61.0	62.7	0.62			
	B3D	52.4	67.4	1.24	2.40	100.1	
	B4D	62.2	67.6	1.30			
	B5D	199	210	1.99	3.65	100.0	
	B6D	121	140	1.78			

a. Samples collected during the period 10/23/78 to 11/28/78.
b. Calculated using mean of MTB and AIHL method results from the first extraction, expressed as a percent.
c. Excluded from mean.
d. Mean of two values.

Table 7

Recovery of Sulfate and Efficiency of Extraction with Lo-Vol Teflon Filter Samples from Los Angeles [a]

Method	Filter Code[b]	µg $SO_4^=$ from First Extraction AIHL	µg $SO_4^=$ from First Extraction MTB	µg $SO_4^=$ in Residual Extract Wetting Filter	µg $SO_4^=$ in Second Extract of Filter Pair by IC	Average Extraction Efficiency for Filter Pair[b]	Mean (C.V.%) Extraction Efficiency for Method
Mechanical Shaking	L1A	64.0	68.2	0.06	19.1	88.3	92 (5.8)
	L2A	74.1	77.4	0.21			
	L3A	111	124	0.25	4.60	97.7	
	L4A	61.0	64.0	0.21			
	L5A	64.0	72.0	0.30	28.2	88.8	
	L6A	144	157	0.28			
Ultrasonic with MeOH	L1B	92.0	95.8	0.01	3.90	98.4	92 (6.1)
	L2B	138	146	0.04			
	L3B	126	138	0.01	31.2	87.8	
	L4B	86.9	94.0	0.19			
	L5B	152	159	0.00	34.0	89.8	
	L6B	139	149	0.05			
Ultrasonic	L1C	123	136	0.08	31.0	89.0	87 (2.2)
	L2C	115	124	0.15			
	L3C	33.0	32.2	0.03	31.4	87.5	
	L4C	178	190	0.42			
	L5C	109	116	0.37	24.7	85.2	
	L6C	28.2	27.0	0.08			
Heating in 80°C	L1D	17.7	24.0	0.17	12.6	83.9	80 (5.1)
	L2D	42.1	48.4	0.09			
	L3D	39.7	43.6	0.17	16.8	79.5	
	L4D	21.8	22.4	0.14			
	L5D	54.4	47.4	0.24	33.3	75.8	
	L6D	43.0	44.4	0.42			

a. Samples collected during the period 11/1/78 to 11/13/78.
b. Calculated using mean of MTB and AIHL method results from the first extraction, expressed as a percent.

the Berkeley samples proved to be more heavily loaded with sulfate. With the Berkeley samples, efficiencies were > 98% by all methods. However, the Los Angeles samples appeared to be more difficult to extract for sulfate, with method (4), heating at 80°C, significantly less efficient than the other procedures. The latter averaged about 90%. The use of methanol to pre-wet the filters did not produce a consistent improvement in efficiency. The choice between mechanical shaking and ultrasonic extraction can probably be based on convenience and personnel costs.

The lower efficiency for extraction of Los Angeles vehicular effluent-enriched samples compared to those from Berkeley parallels the results for hi-vol samples (Section III); the reduced efficiency may reflect the influence of oily particulate matter (e.g. aerosolized lubricating oils) in encapsulating other particulate constituents. Alternatively, elevated levels of relatively insoluble lead sulfate might contribute to reduced recoveries of sulfate in initial extractions. However, assuming the solubility product for pure $PbSO_4$ in water, 1.8×10^{-6}, to be applicable to the atmospheric sample, then for reasonable levels of $PbSO_4$ (e.g. < 50% of the total Pb) lead sulfate formation would not be a significant source of reduced sulfate recovery.

V. STABILITY OF PRE-MIXED REAGENT FOR TURBIDIMETRIC SULFATE ANALYSIS

A. Introduction

The barium sulfate turbidimetric methods (AIHL Methods 61 and 75) employ a pre-mixed reagent composed of glycerol, HCl and water for stabilizing the colloidal suspension. A ruggedness test performed during the previous phase of this grant[3] compared freshly prepared reagent with a batch prepared two years earlier. The results indicated that the choice of the old or new reagent was the source of 78% of the total variance observed, a result which exceeded the variance of the dummy variable at the 95% confidence level.

Based on these results, the stability of this reagent on storage was evaluated. For this purpose a batch of reagent prepared in October 1977 was used periodically to prepare working curves for turbidimetric analysis. Changes were sought in slopes, intercept and standard error of the estimate, $S_{y \cdot x}$, from linear regression for standards in the range 300-1600 µg/20 ml samples.

B. Results

Results with the three parameters are plotted against reagent age in Figures 2-4. The working curve slope, sometimes defined as the sensitivity of the method, displayed no significant trend over about 15 months. Over this period, the intercept increased slightly. The most interesting results are those for $S_{y \cdot x}$. Except for the cluster of data at about 200 days, $S_{y \cdot x}$ remained approximately constant. The exception was associated with the use of a different B & L Model 20 spectrometer, the usual instrument being temporarily unavailable. Thus the precision of results may be influenced by the instrument used.

EFFECT OF PRE-MIXED REAGENT AGE IN TURBIDIMETRIC SULFATE ANALYSIS
WORKING CURVE SLOPE VS. TIME

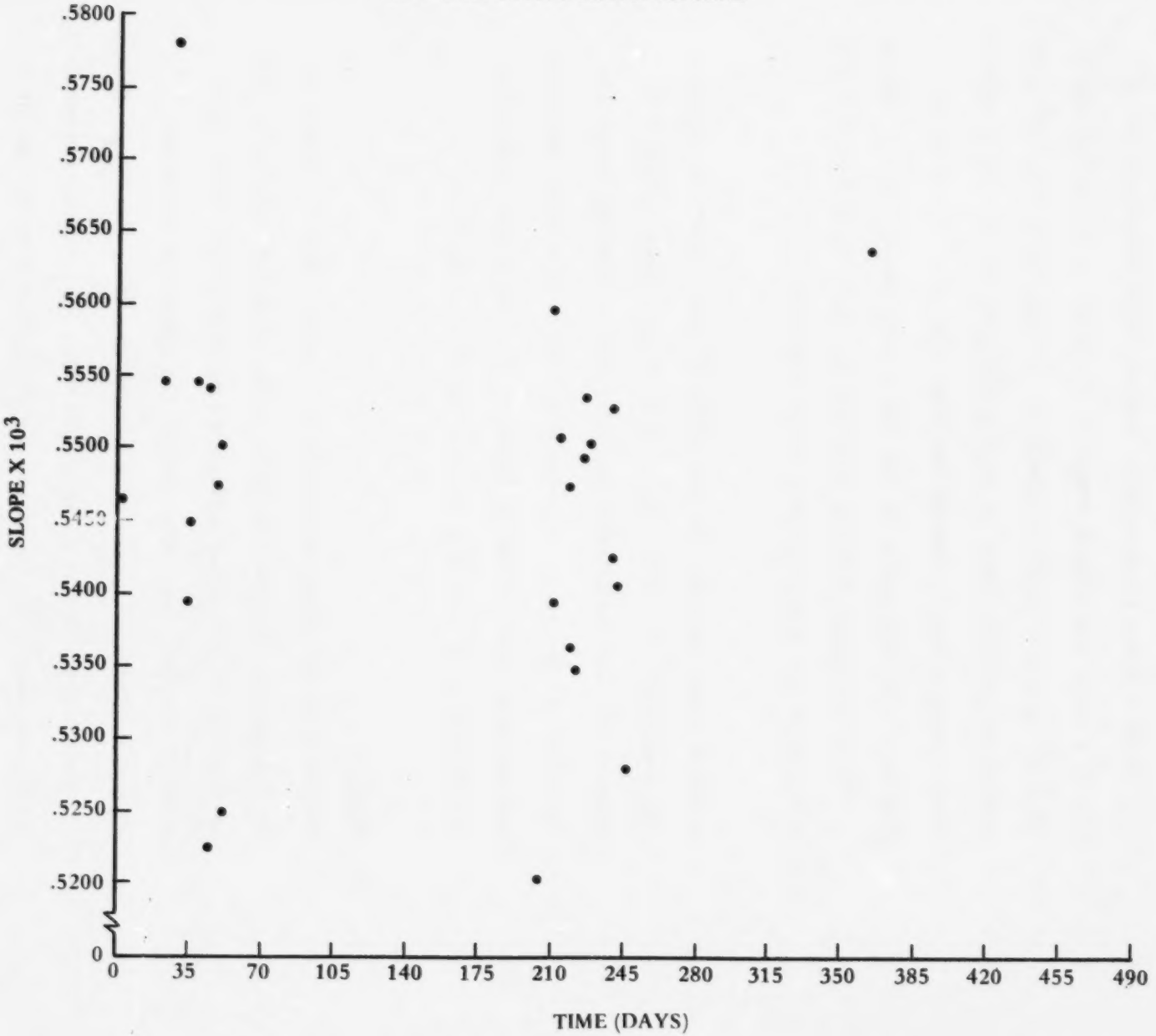

Figure 2

EFFECT OF PRE-MIXED REAGENT AGE IN TURBIDIMETRIC SULFATE ANALYSIS
WORKING CURVE INTERCEPT VS. TIME

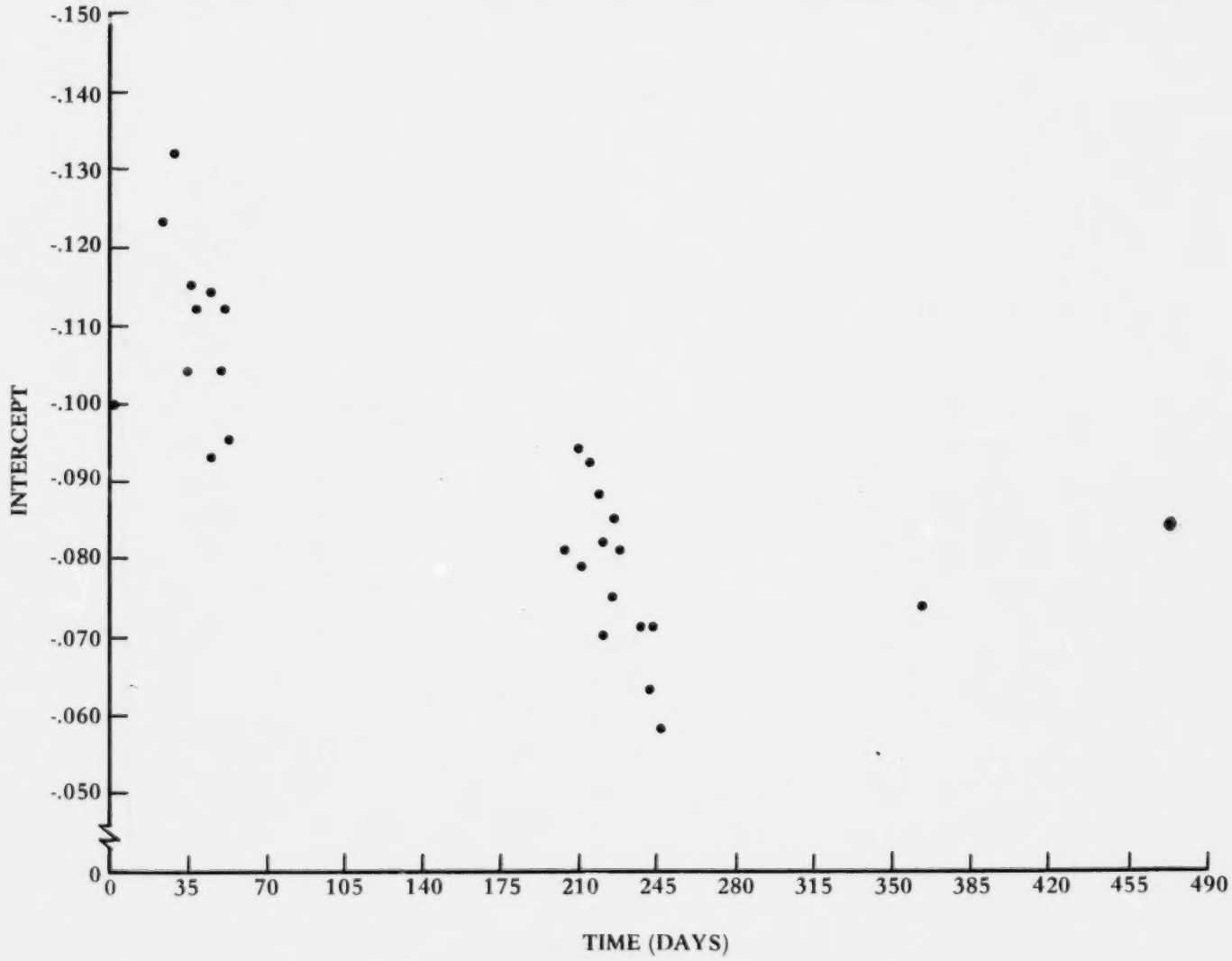

Figure 3

EFFECT OF PRE-MIXED REAGENT AGE IN TURBIDIMETRIC SULFATE ANALYSIS
WORKING CURVE Sy.x VS. TIME

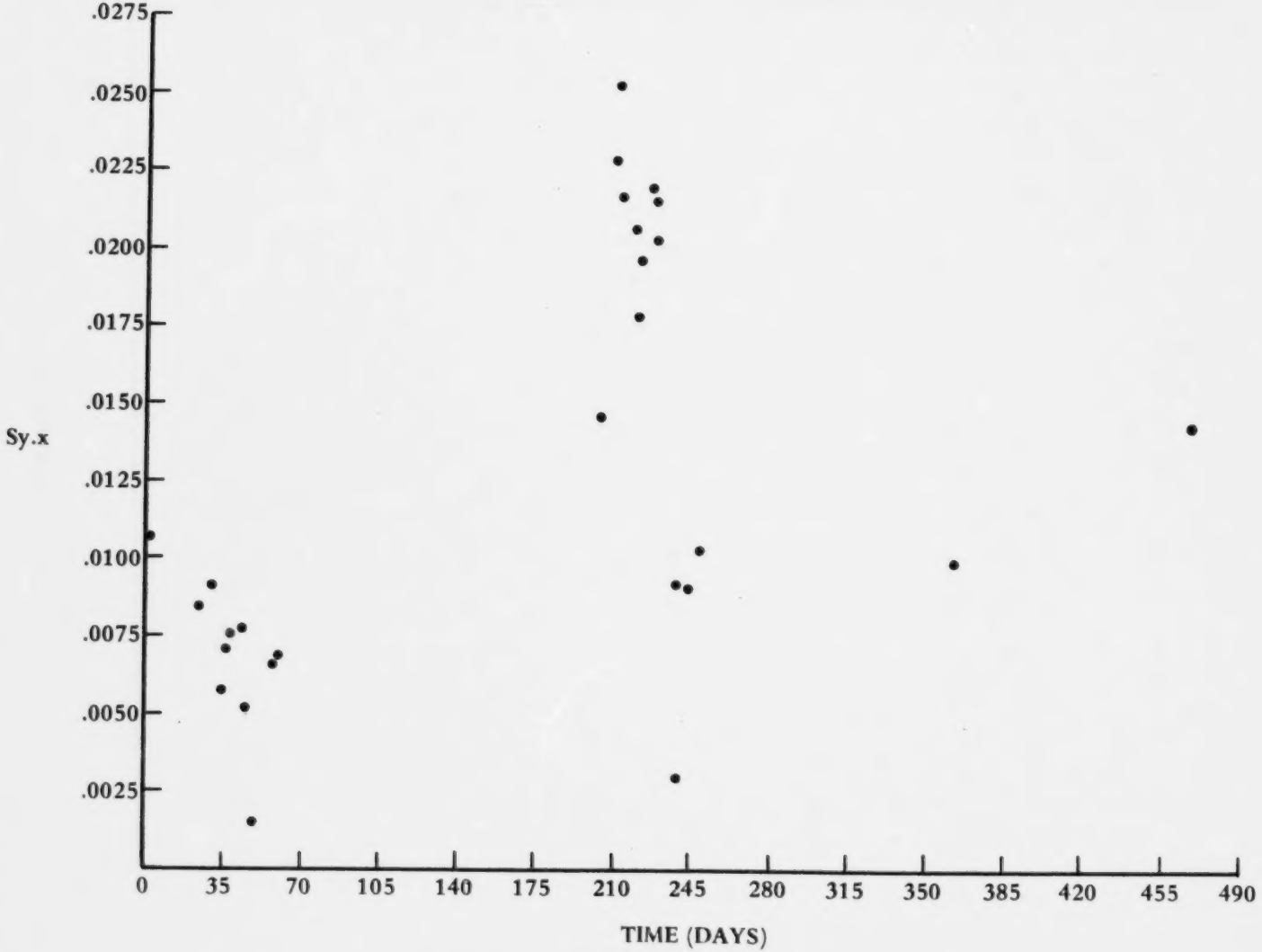

Figure 4

C. Conclusions

The shelf-life of the pre-mixed reagent is at least 15 months. The sensitivity of the method to choice of 2-year old or a new reagent in the previously performed ruggedness test may have been due to factors other than aging (e.g. contamination).

VI. EVALUATION AND IMPROVEMENT OF A TURBIDIMETRIC METHOD FOR SULFATE USING SULFAVER IV^{R}

A. Introduction

Preceding studies under this Grant[3] included development of a protocol utilizing SulfaVer IV^{R}. Accuracy and precision with EPA sulfate audit strips, working range, and agreement with other methods were also determined. The current program has provided additional evaluation of this technique employing a ruggedness test[17] to optimize the method and an intermethod comparison with the optimized procedure.

B. Ruggedness Test

The ruggedness test protocol followed is similar to that given in Appendix C of Reference 3. The eleven factors evaluated are given in Table 8. Factors B and F, organics and colloidal clay, were included because prior studies of other turbidimetric sulfate methods indicated these to be interferents.[3] The levels of organics used, absorbance 0.025 and 0.1 per cm at 400 nm, compares to a maximum value of 0.07 per cm observed for extracts from St. Louis samples. The levels of colloidal clay, 200 and 1000 µg kaolinite/20 ml, compare to a maximum 90° light scattering (at 600 nm) for St. Louis extracts, expressed in the corresponding clay concentration, of 1300 µg/20 ml, following filtration through a fine glass frit. All samples were mixed with SulfaVer IV^{R} and their absorbances determined in the same container, thereby avoiding potential errors introduced with multiple transfers (c.f. AIHL Methods 61 and 75, Reference 3).

Table 8

FACTORS FOR EVALUATION IN RUGGEDNESS TEST OF SULFAVER METHOD[a]

Factor	Low (-)	High (+)
A = Spectrophotometer	B & L Model 20	B & L Model 21
B = Organics concentration[b]	Absorbance 0.025/cm at 400 nm	Absorbance 0.1/cm at 400 nm
C = HCl concentration	Zero	0.3 N
D = Reaction time	5 minutes	20 minutes
E = Sulfate level	300 µg/20 ml	1300 µg/20 ml
F = Colloidal clay level[c]	200 µg/20 ml kaolinite	1000 µg/20 ml kaolinite
G = Loss of SulfaVer	Discard 50% of SulfaVer from each pillow	Discard no SulfaVer
H = Shaking speed[d]	270 oscillations/minute	90 oscillations/minute
I = Shaking time	3 minutes	1 minute
J = Reaction vessel and spectrophotometer cell	Screw cap test tube (25 x 150 mm)	Cuvet (25 x 150 mm)
K = Dummy		

a. Concentrations and absorbances shown are for 20 ml samples prepared to simulate hi-vol filter extracts.

b. Yellow organics isolated from hi-vol filter aqueous extractions as described in Appendix G, Reference 3.

c. Used to simulate the source of turbidity seen in some filter extracts.

d. Using an Eberbach platform shaker.

The mean results of each of the twelve experiments, each run three times, calculated by third order regression for the working curve, were expressed as the ratio of the observed to the theoretical sulfate level. The effect of each factor was evaluated as the difference between mean results for the runs with high (or plus) and low (or minus) levels. Table 9 ranks the observed effects, squares the effects to estimate the variance of the method due to that effect and determines the proportion of the total due to each factor.

The results show the most significant sources of variability in result to be the sulfate level and the choice of spectrophotometer. At the low sulfate level (300 µg/20 ml) results averaged about 30% high causing the measured effect for Factor E to be substantially negative. The substantial variance observed for Factor A (choice of spectrophotometer) followed from average results by the B & L 21 which were 26% too high compared to about 3% too low with the B & L 20. We believe this reflects primarily an interaction with the effect of sulfate and interferent levels; the results for Factor A are strongly influenced by the results for three runs at 300 µg/20 ml sulfate (Runs 4, 5 and 10). It is more reasonable that the high results in these three runs (average 48% positive error) resulted from the relatively high interferents and low sulfate levels rather than selection of spectrophotometer. The value for $S_{y \cdot x}$, the standard error of the estimate , for the working curve for six trials was (7.9 to 22) x 10^{-3} with the B & L 21 and (13 to 21) x 10^{-3} with the B & L 20. Thus the degrees of scatter were about equal with the two instruments. Results for Factor A are, therefore, considered to be insignificant. Results for other

Table 9

RESULTS OF RUGGEDNESS TEST OF SULFATE ANALYSIS BY TURBIDIMETRY

Factor	Identification	E	E^2	E^2 as % of Total
E	Sulfate level	-0.326	0.106	41.3
A	Spectrophotometer	0.275	0.0753	29.3
I	Shaking time	0.153	0.0233	9.1
G	Loss of SulfaVer	0.129	0.0166	6.5
K	Dummy	-0.115	0.0131	5.1
B	Organics concentration	0.104	0.0107	4.2
D	Reaction time	-0.0758	0.0057	2.2
C	HCl addition	-0.0645	0.0041	1.6
F	Colloidal clay	-0.0341	0.0011	0.4
H	Shaking speed	-0.0285	0.0008	0.3
J	Reaction vessel and cell	0.0133	0.0001	0.04

E = Effect of variable = difference between mean results for runs with high (or plus) and low (or minus) levels.

factors differ from those for the dummy factor by less than a factor of two or show variance less than that of the dummy. Therefore, only sulfate level (Factor E) is considered to be a significant source of variance.

It may be noted that discarding half of the contents of the SulfaVer IV^{R} pillows had no significant effect on results. In trials with 10 pillows, the variability (C.V.) in contents transferred to the samples was 10%. Thus loss of 50% would be greater than would ever be expected. Clearly, the quantity of reagent is in large excess compared to that required at up to 1300 µg/20 ml.

C. Comparisons with Prior Study

The preceding study of the SulfaVer IV^{R} method employed an analytical procedure analogous to that in AIHL Method 61, (i.e. reagent and sample were mixed in graduated cylinders and transferred to 2 cm cylindrical cuvets for turbidity measurement with a B & L Model 70 spectrophotometer). This procedure yielded recoveries within 10% of the theoretical sulfate values using EPA audit strips in the range 300 to 1700 µg/20 ml, with a C.V. < 6%. Furthermore, the working range, based on precision and relative accuracy of a single atmospheric extract diluted to various concentrations, was determined to be from 180 to at least 1400 µg/20 ml (accuracy within 4%, C.V. $\leq$ 6%). Finally, in analysis of 24 atmospheric hi-vol filter samples, a median C.V. of 5.3% was found.

The present ruggedness test showed positive error of about 30% at 300 µg/20 ml with Factor J (reaction vessel and cell) without significance. However, in contrast to the evaluation of accuracy, precision and working range described above, all solutions in the

ruggedness test contained added colloidal clay (200 or 1000 µg/20 ml) and yellow organics (absorbance 0.025 or 0.1/cm at 400 nm). While the atmospheric extract previously used to determine working range also showed absorbance at 400 nm, when diluted to provide $\leq$ 300 µg sulfate/20 ml the absorbance was below 0.025 cm^{-1} at 400 nm, the lower level in the ruggedness test due to organics. Thus the results from the ruggedness test are probably not in conflict with the prior work.

Aside from the problem of accuracy, the lack of significant sensitivity of the method to the level of colloidal clay appears surprising. However, in interference studies employing barium chloride-glycerol-HCl-H_2O (e.g. AIHL Method 75) for sulfate analysis by turbidity, with 750 to 1200 µg/20 ml sulfate, a change from 200 to 1000 µg/20 ml colloidal clay (kaolinite) caused only a 9 to 12% decrease in observed sulfate. The effect of this change in clay concentration at 200 µg/20 ml sulfate was, however, large (-82%). If the change at 300 µg/20 ml sulfate, as used in the ruggedness test, were similar to that at 200 µg/20 ml, then a significant variance due to Factor F would be expected. Further work is needed to explore interference effects with the SulfaVer IV^R method.

D. Procedure for Sulfate Analysis with SulfaVer IV^R

Based on prior studies and the ruggedness test, a procedure has been prepared (AIHL Method 79) suitable for sulfate analysis of 24-hour high volume filter samples. It is included as Appendix G. The extraction procedure specified, mechanical shaking at room temperature, is based on results obtained in Section III.

VII. STUDIES WITH THE DIONEX MODEL 10 ION CHROMATOGRAPH

A. Introduction

During the preceding phase of this grant the Dionex Model 10 ion chromatograph (IC) was evaluated for use in analyzing hi-vol filter samples. The principal focus of IC studies in the current grant period was on evaluating its use with smaller samples such as obtained with low-volume, dichotomous samplers. Two approaches were evaluated, a larger sample loop and a sample pre-concentrator. In addition, the system was modified by replacing the 500 mm anion separator column with one of 250 mm length to reduce analysis time.

Before beginning work at lower sulfate ranges, the problem of interference effects by nitrate and drifts in calibration curves[3] was re-examined.

B. Data Reduction Techniques and Interference Effects of Nitrate on Sulfate Determination

Previous studies directed toward analysis of hi-vol filter samples established a 2-3% positive interference in sulfate measurement when nitrate was present at equal concentration (by weight). This interference was observed using peak heights measured from an extrapolated base line (Figure 5A). Before modifying the IC for lo-vol sample analyses, interference effects were evaluated at higher $NO_3^-/SO_4^=$ ratios with data reduction by the previously used peak height method as well as the trailing peak and integration techniques (Figure 5A-C).

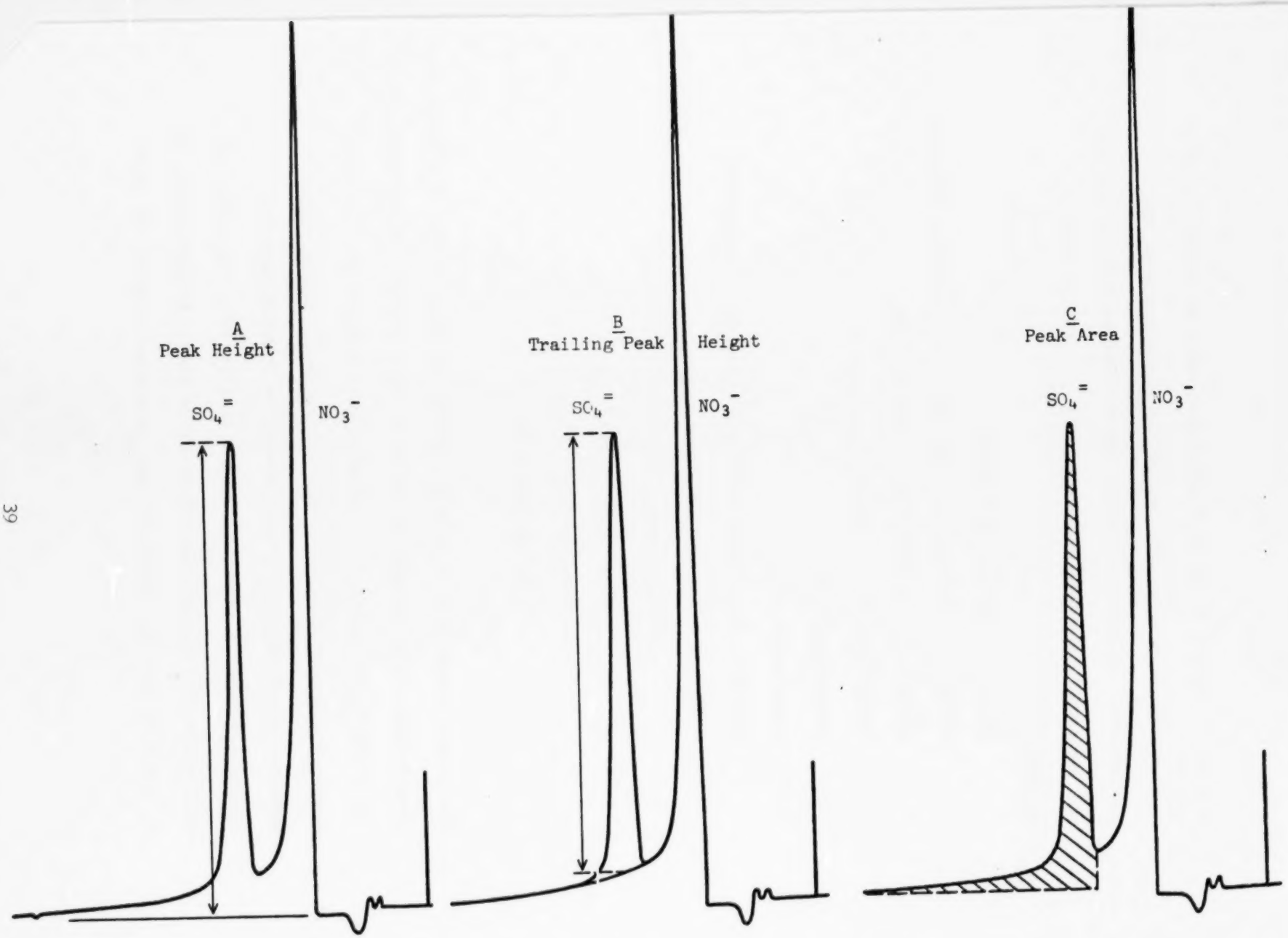

Figure 5 SULFATE DATA REDUCTION PROCEDURES FOR IC.

For this study the IC was calibrated twice each day using standards without nitrate and the data reduced using the corresponding calibration. As discussed below, the calibration shift within one day was usually significant. Experimental conditions were as follows:

Range: 10 μmho (linear scale)

Column: 3 x 100 mm precolumn and 3 x 500 mm anion separator

Eluent: 0.0024 M Na_2CO_3 + 0.0030 M $NaHCO_3$

Eluent Flow Rate: 2.5 ml/min

Sample Loop: 30 μl

Temperature: 35°C

Recorder: 1.0 V full scale (equivalent to Dionex meter)

Integrator: Autolab Minigrator set for

peak width = 99

sensitivity = 99999

baseline = 1.0

trailing peak = 0.0

The results summarized in Table 10 confirm the significance of nitrate interference using the peak height method with extrapolated baseline. Use of the trailing peak and peak area methods yield reduced error. However the precision of the trailing peak height method appears somewhat better compared to peak areas. We conclude that for atmospheric samples containing nitrate at concentrations $\geq$ that of sulfate the trailing peak method should be used. Alternatively, the IC should be operated to achieve base line separation of the peaks.

Table 10

Interference Effect of Nitrate on Sulfate Determination

$SO_4^=$ (µg/ml)	NO_3^- (µg/ml)	(% Error)[a] Peak Height[b]	Trailing Peak[c]	Peak Area
20	40	+ 11.1	+ 1.3	+ 9.2
20	40	+ 6.1	- 1.3	---[d]
20	40	+ 8.8	- 0.2	- 1.0
20	40	+ 6.7	- 0.7	+ 7.0
	Mean:	+ 8.2 ± 2.3	- 0.2 ± 1.1	+ 5.1 ± 5.4
20	60	+ 10.6	- 0.9	+ 5.6
20	60	+ 10.9	- 1.3	- 3.4
20	60	+ 8.2	- 0.7	- 0.7
	Mean:	+ 9.9 ± 1.5	- 1.0 ± .3	+ 0.5 ± 4.6
20	100	+ 16.5	+ 0.3	+ 4.2
20	100	+ 15.1	- 2.3	- 6.0
20	100	+ 14.6	+ 2.3	- 1.6
	Mean:	+ 15.4 ± 1.0	+ 0.1 ± 2.3	- 1.1 ± 5.1
40	80	+ 7.3	0.0	+ 3.2
40	80	+ 6.7	- 0.4	- 0.5
40	80	+ 4.7	- 2.0	+ 2.4
	Mean:	+ 6.2 ± 1.4	- 0.8 ± 1.1	+ 1.7 ± 2.0
40	120	+ 10.6	+ 0.3	+ 2.5
40	120	+ 8.8	- 0.7	- 0.3
40	120	+ 7.5	- 1.0	+ 0.4
	Mean:	+ 9.0 ± 1.6	- 0.5 ± .7	+ 0.9 ± 1.5
80	160	+ 7.5	+ 1.4	---[d]
80	160	+ 4.4	- 0.8	---[d]
80	160	+ 4.2	- 0.6	---[d]
	Mean:	+ 5.4 ± 1.9	0.0 ± 1.2	

a. 100 x (Observed-True)/(true)
b. From extrapolated base line (Figure 5A)
c. See Figure 5B.
d. Integrator did not function correctly.

Aside from partial overlap of the sulfate and nitrate peaks it was considered possible that the presence of nitrate might increase the sulfate peak by reducing its retention time and, therefore, sharpening the peak. The influence of nitrate on sulfate retention time is shown in Table 11. Results are from data obtained on a single day and, except as noted are means $\pm$ 1 σ for two trials. The data indicate no significant effect of nitrate on sulfate retention time. Furthermore, increasing sulfate concentration, alone, did not influence retention time.

C. Accuracy of Sulfate Determination by IC and the Effect of Shifting Calibration Curves

Preceding studies demonstrated a persistent positive bias in sulfate determinations using EPA sulfate audit strips. The positive error was especially pronounced for a sample with $NO_3^-/SO_4^=$ weight ratio of ca. 2. Since the reported accuracy might have been influenced by the method of data reduction (the peak height method as shown in Figure 1A), a set of audit strips was extracted (30 minutes ultrasonic) and analyzed by IC using the trailing peak method. Instrument conditions were as given in section (A) above. Two calibration curves were obtained daily from three sulfate standards (10, 20 and 40 µg/ml). Data from samples was reduced using the most recent calibration. Results from analysis of the audit strips are given in Table 12. Consistent with prior observations the 9000 series samples with high nitrate levels showed the largest positive error. However the mean ratio, observed/theoretical of 1.03 for this series by peak heights compares to 1.15 previously reported.

Table 11

The Effect of Nitrate on Sulfate Retention Times

$SO_4^=$ (µg/ml)	NO_3^- (µg/ml)	$SO_4^=$ Retention Time (seconds)
10	0	540[a]
20	0	538 ± 5
20	40	539 ± 0
20	60	539 ± 0.7
20	100	545 ± 9
40	0	537 ± 2.8
40	80	539 ± 5
40	120	541 ± 4
80	0	534 ± 11
80	160	529 ± 0

a. Single trial

Table 12

ANALYSIS OF EPA SULFATE AUDIT STRIPS BY THE DIONEX IC[a]

Sample	Theoretical Value ($\mu g\ SO_4^{=}$/ml)	$SO_4^{=}/NO_3^-$ Wt. Ratio	Mean Observed Value (µg/ml) Pk Ht	Tr Pk	Pk Area	C.V. (%) Pk Ht	Tr Pk	Pk Area	Observed/Theoretical Pk Ht	Tr Pk	Pk Area
712-7000 Series	10.0	4.2	10.1	10.1	10.0	3.1	3.1	5.3	1.01	1.01	1.00
9000 Series	14.9	0.60	15.3	14.6	14.3	3.9	3.0	3.9	1.03	0.98	0.96
712-5000 Series	45.0	2.8	44.5	43.9	44.2	1.6	1.6	1.2	0.99	0.98	0.98

a. Results are means for four strips from each series extracted by 30 minutes ultrasonic extraction in 50 ml water.

The peak height technique gave slightly higher results than with the other techniques. None, however differed, on average by more than 4% from the true values. Precision, as measured by coefficients of variation for four strips, was approximately equal by all techniques.

The above results suggest that something other than nitrate interference was the dominant cause of the positive errors previously reported. In seeking this cause we have evaluated changes in the instrument response within one day's operation which could lead to shifts in calibration curves. Table 13 indicates the shifts observed. In all cases the change is in the direction of increased instrument response. The magnitude of the shift is from 4 to 17% over 2-3 hour periods and affects both peak heights and areas. The variability of the shift appears to depend upon operating parameters such as eluent flow rate. For example, increasing eluent flow rate increases the rate of depletion of the suppressor column, resulting in a faster calibration shift per unit time. The rate of change is also high just after and prior to suppressor column regeneration, and after the pump is shut off for any reason. Thus, depending on the time between calibration and sample analysis a given sample would show varying error but usually in the positive direction. We consider this change in calibration to be the principal source of positive errors in sulfate analyses with IC.

Discussions with E. Johnson, Dionex Corp. indicate that this phenomenon may relate to changes in retention of protonated sulfate on the suppressor column. As the protons of the suppressor column are replaced by sodium from the eluent, the resulting neutralized

Table 13

CHANGE IN PEAK HEIGHT AND AREA WITH TIME WITH SULFATE STANDARDS[a]

$SO_4^=$ (µg/ml)	First Calibration[b]		Second Calibration[b]		Change in Calibration (%)	
	Pk. Ht.	Pk. Area	Pk. Ht.	Pk. Area	Pk. Ht.	Pk. Area
10	8.0	1978527	8.4	2178198	+ 5.0	+10.1
	7.1	1881778	8.3	2108238	+16.9	+12.0
20	16.2	3992628	17.7	4289327	+ 9.3	+ 7.4
	15.2	3787132	16.8	4171439	+10.5	+10.2
40	34.8	8436753	36.7	8771102	+ 5.5	+ 4.0
	32.2	7748065	35.7	8502336	+10.9	+ 9.7

a. Results shown for two trials made on successive days.

b. Interval between calibrations 2-3 hours.

resin exhibits an affinity for the HSO_4^- ion. The result, he suggests, is to sharpen somewhat the sulfate peak leading to increased peak height. However, peak areas should not, in principle, be affected in contrast to our observations. Peak areas, Johnson notes, are inherently less precise to use with a pulsing chromatographic system compared to peak heights. He recommends installing a long section of Teflon tubing to attenuate pump pulses and then to use peak areas. Since in our work peak areas have no clear advantage regarding accuracy and in our previous studies have been found somewhat less precise, the peak area technique will not be used.

There appears to be sources of negative drift in the instrument response as well (e.g. temperature decreases in the eluent supply which was not thermostated). These may, occasionally, partially or completely offset the positive drift associated with consumption of the suppressor column.

D. Sulfate Analysis Using a Pre-concentrator Column

1. Introduction

The sample pre-concentrator column (SPC) consists of a length of glass tubing, approximately 50 mm long, of which 35 mm is packed with anion resin of the type used in the separator columns. Like the latter columns, the SPC is 3 mm in I.D. and has Altex-Durrim plastic fittings, with about 100 mm lengths of Teflon tubing on each end, for connection to the slide valve in place of the usual sample loop. The volume of the column and tubing is about 0.25 ml.

In use, one injects the sample through the sample port, passing it through the resin, which retains and separates to some degree the anions from the sample. Then the slide valve is switched so that the eluent passes through the SPC, eluting out the collected ions. The analysis then proceeds as usual.

2. Advantages

The advantages of the pre-concentrator compared to the 30 µl sample loop previously used are:

a. The ability to analyze very low sulfate concentrations since the total in a large sample (e.g. 15 ml) can be analyzed. For example, samples of distilled water were determined to have 0.004 to 0.01 µg sulfate/ml by this technique.

b. Unlike the loop, sample volume is easily varied. Thus if a sample exceeds the working range a smaller aliquot is injected rather than having to dilute the sample.

3. Disadvantages and Problems Encountered

a. The pre-concentrator had to be regenerated after about 125 samples (using a solution containing 0.5N each of $NaHCO_3$ and Na_2CO_3).

b. Injection of sample from the pre-concentrator causes a mementary drop in line pressure and, therefore, eluent flow rate. As a result, one or more spurious positive peaks occur initially, followed by a negative peak about a minute later.

c. Sample injection is more complex; a syringe is first loaded with a known volume of sample and injected followed by an injection of distilled water to flush the syringe, tubing and SPC to insure all sample is on the resin.

d. Manual injections of relatively large volumes are made against a large back pressure leading to operator fatigue. Dionex recommends use of a pump.

e. After about 100 injections the resin in the pre-concentrator had been compressed to about one-half its initial volume. This increased the back pressure and created more free void in the glass tubing.

4. Procedure for Sample Injection Using the Sample Pre-concentrator Column (SPC)

The procedure adopted for sample injection with method evaluation studies and sample analyses is as follows:

a. Equipment

(1) Disposable syringe, 12 cc volume, "Monoject", Sherwood Medical Industries or equivalent, used without a needle.

(2) Adjustable dispensing pipet, Pipetman, or equivalent, providing ca. 1% precision over desired range.

b. Set the pump so that the minimum pressure during injection is 50 to 100 psi, consistent with an acceptable eluent flow rate.

c. Set the injector switch to "Load" position. Inject 2.0 ml of distilled water through the SPC with the syringe.

d. Draw in 3 ml minus sample aliquot of distilled water into the syringe.

e. Using the pipet, dispense the sample aliquot (0.10 ml to 3.0 ml) into the tip of the syringe. For this, the pipet tip must fit inside and seal the syringe. Inject the sample into the SPC.

f. Carefully withdraw the syringe from the port and draw in another 3.0 ml of distilled water* and inject this into the port.

g. After the baseline is stable, set the injection switch to "Inject". After 2.0 min, flip the switch to "Load".

h. If a spurious negative or positive peak (due to injection) interferes with the elution of the sample peaks, change the time in g. above to eliminate this problem.

---

*The total amount of distilled water is not critical but should be minimized to decrease operator fatigue and compression of the SPC resin.

5. Test Operation Parameters

Range: 30, 100 and 300 μmho (linear scale)

Columns: 3 x 100 mm precolumn + 3 x 250 mm anion column

Eluent: 0.0030 M $NaHCO_3$ + 0.0024 M NO_2CO_3

Elution rate: 2.5 ml/min

Recorder: 0.20 and 1.0 volt full scale

Bath: 35°C and ambient

Integrator: As given in Section A

6. Range and Precision

The ranges used, the resulting approximately 80% of full scale sulfate level, and our typically obtained error are given in Table 14. Figure 6 illustrates a working curve for analysis of low concentration sulfate samples.

7. Nitrate Interference in Sulfate Analysis

Using sulfate samples in the 0-2 μg range with nitrate/sulfate ratios of 2 w/w, the error in sulfate by the trailing peak height method averaged 1.8%, and by peak areas, 5.8%.

8. Atmospheric Sample Analysis

Because of its potential for analysis of very low concentration samples, the Dionex with pre-concentrator was used for analyses of extracts obtained in studies comparing extraction procedures for low-volume Teflon filter samples. Results from the analyses are included in Section IV.

Table 14

Instrument Settings, Sulfate Level for 80% Full Scale and Accuracy[a] with Standards Using the Dionex IC with Pre-concentrator

Instrument Range μmho	Recorder Full Scale, volts	Effective Range, μmho[b]	Approx. 80% Full Scale Sulfate, μg	Mean Error	
				Peak Ht.	Peak Area
100	1.0	100	40	3.9	4.3
300	0.2	60	20	3.4	4.8
30	0.2	6	2	1.9-7.7[c]	2.0-7.4[c]

a. Measured by the mean of the absolute values for percent differences between the true sulfate concentrations used for calibration and the values obtained by linear regression of the working curve constructed between 10 and 100% of the 80% full scale sulfate value shown.

b. Effective range, in μmho, equals (Instrument Range) x (Recorder Full Scale Voltage).

c. Range of mean values from three trials.

TYPICAL WORKING CURVE FOR SULFATE ANALYSIS BY DIONEX IC WITH PRE-CONCENTRATOR

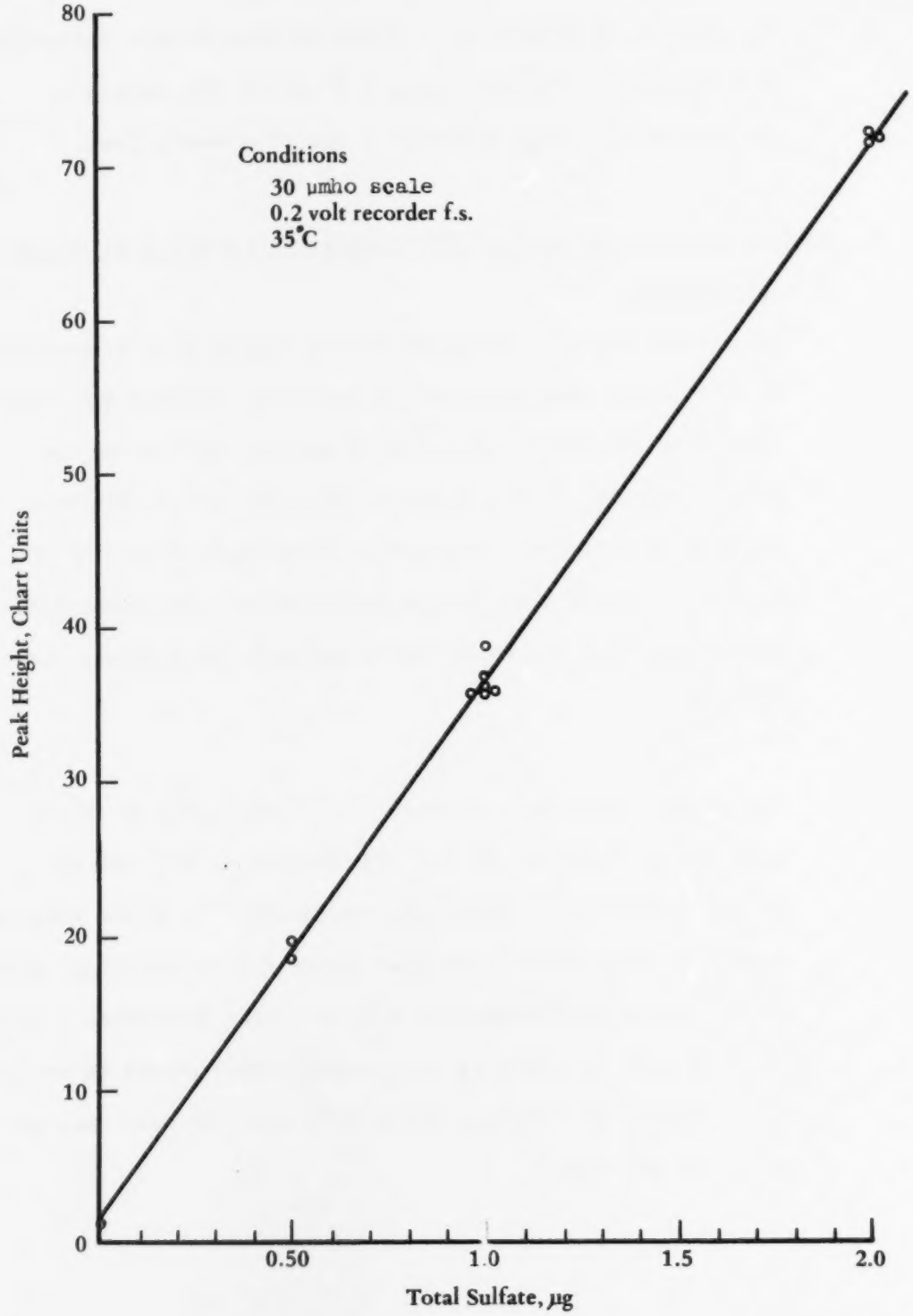

Figure 6

9. Conclusions

The use of a pre-concentrator permits analyses of sulfate samples containing very low (e.g. < 0.1 μg/ml) sulfate levels. However, for analysis of samples to be expected from 24 hour collection with dichotomous samplers (e.g. > 5 μg/ml) this method is unnecessarily complex compared to use of a sample loop.

E. Sulfate Analysis of Lo-Vol Filter Samples Using an 0.5 ml Sample Loop

1. Introduction

For sulfate analysis of lo-vol filter samples such as provided by dichotomous samplers a method providing accurate and precise results in the range 0-20 μg/ml is needed. Increasing the sample loop size from 0.03 to 0.5 ml provided a sufficient increase in instrument sensitivity to accomplish this by IC. As in the studies with the pre-concentrator, the column size was reduced from 500 to 250 mm to decrease the analysis time required.

The present study has evaluated 1) the resolution of anions under these condition, 2) the interference by $SO_3^{=}$ and NO_3^{-}, 3) the linearity and day-to-day reproducibility of the working curves, 4) precision and accuracy using EPA sulfate audit strips, and 5) intermethod comparison with two other procedures. As in previous work the trailing peak height method proved to be the most accurate and precise; the results reported here employed only this procedure.

2. Resolution of Sulfate and Nitrate Related Species

Experimental conditions for this work were as follows:

Range: 100 μmho (linear)

Recorder: 0.5 volts full scale

Columns: 3 x 100 mm precolumn + 3 x 250 mm anion column
+ 6 x 250 mm anion suppressor column.

Eluent: 0.0030M $NaHCO_3$ + 0.0024M Na_2CO_3

Elution Rate: 2.5 ml/min

Column and Detector Temperature: 35°C

Sample Loop: 0.5 ml

(A detailed procedure for IC of samples is included in Appendix H)

Under these conditions, retention times for sulfate, nitrate and nitrite were as given in Table 15. With the shorter separator column, nitrite, nitrate and sulfate are still separated. The retention time difference for sulfate and nitrate, 88 seconds, compares to 160-179 seconds with the 500 mm separator column. Sulfite and sulfate have identical retention times using the standard eluent mixture.

3. The Working Curve for Sulfate Analysis

The working curve for sulfate analysis in the range 0-20 μg/ml is shown in Figure 7. In contrast to results obtained with the 30 μl sample loop, the working curve appears to be distinctly non-linear below 5 μg/ml. The errors in sulfate determination resulting from a regression equation for the best single line are compared to those using a two straight line fit (0-2 μg/ml, 5-20 μg/ml) in Figure 8. For this purpose "observed" values

Table 15

Retention Times for Sulfate, Nitrate and Related Species Using 250 mm Anion Separator Column

Species	Retention Time (sec)	$\Delta\tau$(sec)[a]
nitrite (NO_2^-)	157 ± 5	125
nitrate (NO_3^-)	194 ± 2	88
sulfite ($SO_3^=$)	282 ± 5	0
sulfate ($SO_4^=$)	282 ± 5	---

a. Relative to sulfate.

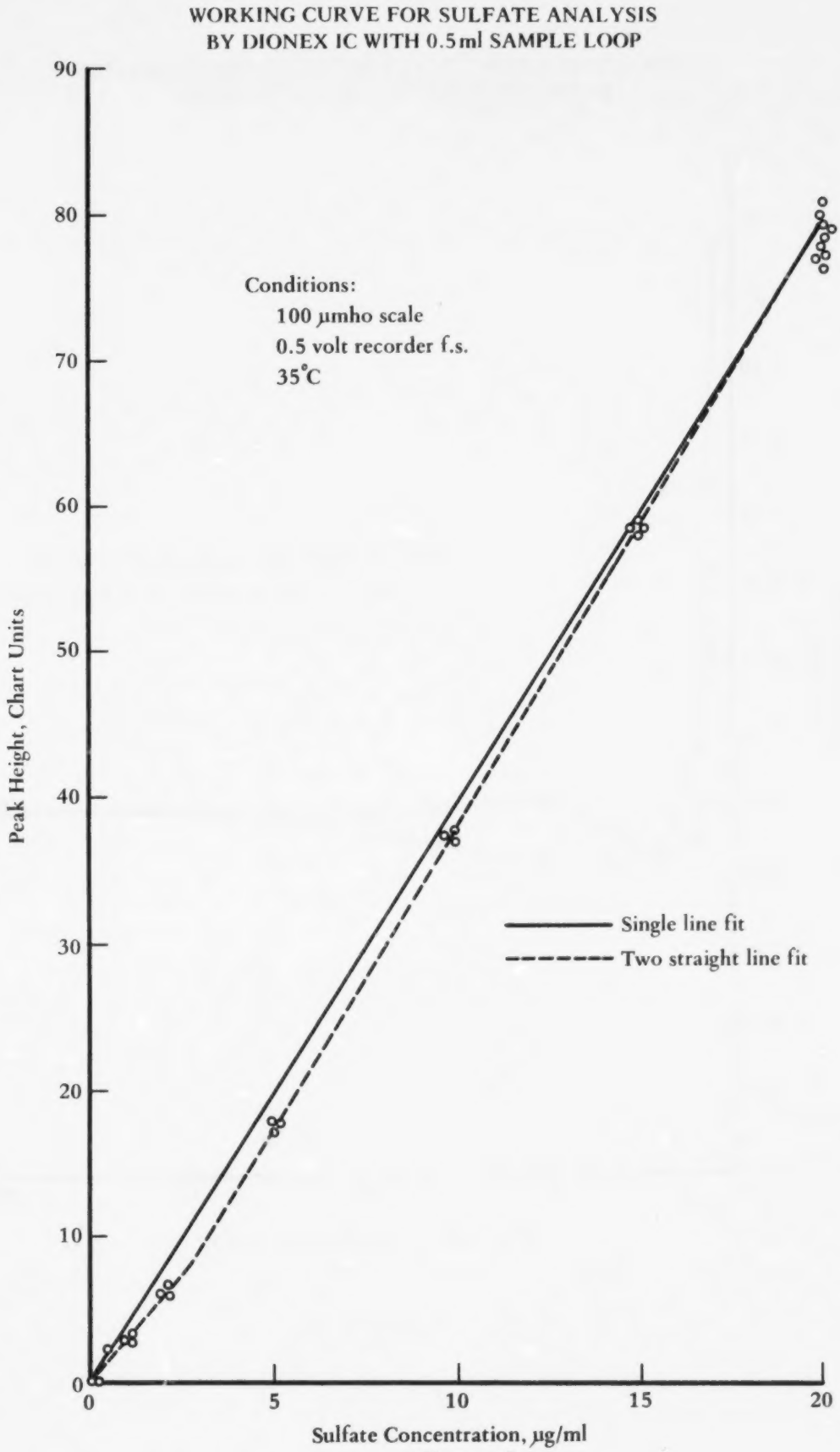
WORKING CURVE FOR SULFATE ANALYSIS
BY DIONEX IC WITH 0.5ml SAMPLE LOOP
Conditions:
100 μmho scale
0.5 volt recorder f.s.
35°C
Single line fit
Two straight line fit
Peak Height, Chart Units
Sulfate Concentration, μg/ml
0
10
20
30
40
50
60
70
80
90
0
5
10
15
20

Figure 7

ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
BY DIONEX IC WITH 0.5 ml SAMPLE LOOP

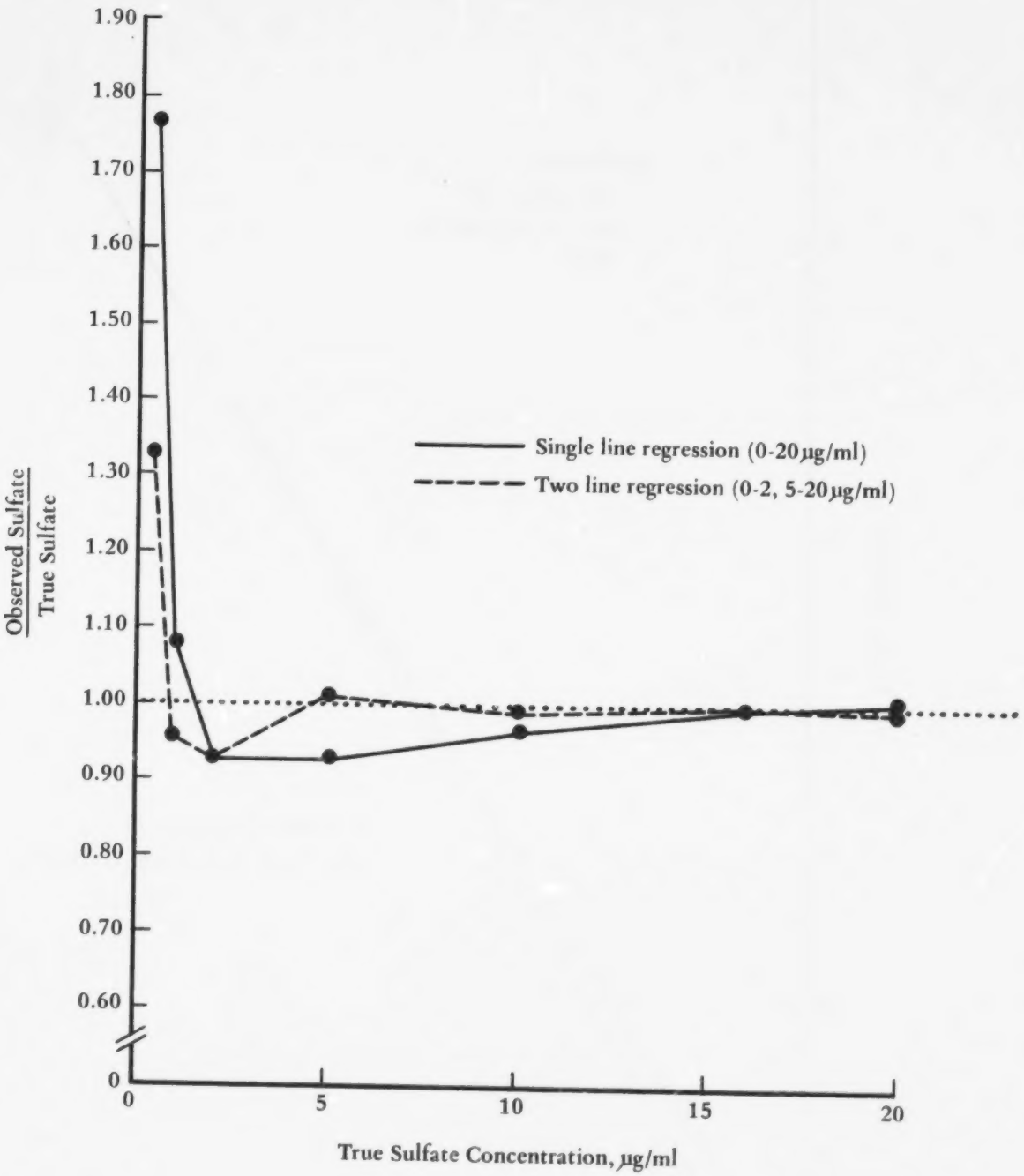

Figure 8

are sulfate concentrations for the standards used in constructing the working curve obtained from the regression equation for the working curve. The ratio of observed to true sulfate levels may be used as a measure of accuracy at varying concentrations. By both procedures, accuracy remains within 10% in the range 1 to 20 µg/ml with errors tending to be negative in the range 1-10 µg/ml. As expected from Figure 7, the difference in accuracy by the two techniques is maximized at 5 µg/ml. Based on these results and the need to minimize numbers of standards run to achieve reasonable sample output, the balance of this study employed two working curves. One was obtained from a straight line regression fit for standards 5 to 20 µg/ml and was used for analysis of samples $\geq$ 5 µg/ml. The second was the straight line based on two points, 0* and 5 µg/ml; it was used for analysis of samples < 5 µg/ml. Where substantial numbers of samples below 5 µg/ml are expected, additional standards in this range should be used.

The day-to-day change in the working curve for the range 5 to 20 µg/ml is given in Table 16. At the time of this work the anion separator column had been used for about 400 samples and thus was nearing the end of its useful life. The relatively large change observed in slope is considered symptomatic of the column age. Within one day's operation, the changes observed were insignificant, however.

*The twice distilled water contained < 0.01 µg/ml sulfate as measured using the sample pre-concentrator.

Table 16

Day-to-Day Change in Working Curve of Dionex IC

Using 250 mm Column for Sulfate Analysis[a]

Date	Slope	Intercept	r	$S_{y.x}$
1 - 3 - 79	3.906	-4.07	0.9991	0.9718
1 - 4 - 79	4.124[b]	-3.40[b]	0.9996[b]	0.7675[b]
1 - 8 - 79	4.654[c]	-3.48[c]	0.9997[c]	0.6383[c]

a. For Standards in the range 5 to 20 µg/ml.

b. Mean of four trials.

c. Mean of two trials.

4. Accuracy and Precision Using EPA Sulfate Audit Strips

Aqueous extracts of EPA sulfate audit strips were prepared by 30-minute ultrasonic extraction and diluted, if necessary, to obtain samples covering the range 2 to 15 µg/ml. Four extracts were prepared for each level. An additional set of four extracts was prepared for 15 µg/ml to provide samples high in nitrate.

The results are summarized in Table 17 and indicate a coefficient of variation of < 5% and accuracy within 15% in all cases. No interference from the high nitrate concentration was seen in the 9000 series samples.

Table 17

Sulfate Analysis of EPA Audit Strips by IC
Using the 0.5 ml Sample Loop[a]

Sample	Theoretical Value (µg/ml)	Wt. Ratio $SO_4^=/NO_3^-$	C.V.(%)	Obs./Theoret.
712-7000 series	2.0[b]	4.2	1.0[d]	0.86[d]
712-7000 series	10.0	4.2	0.8	0.95
9000 series	14.9	0.6	2.8	0.92
712-5000 series	15.0[c]	2.8	5.1	0.92

a. Results are mean values for four extracts at each level using the trailing peak height method. All strips extracted in 50 ml H_2O with further dilution as noted. Working curve based on standards 5, 10, 15 and 20 ml, except as noted.

b. Diluted fivefold.

c. Diluted threefold.

d. Working curve based on standards 0 and 5 µg/ml.

VIII. INTERMETHOD COMPARISONS WITH ATMOSPHERIC SAMPLES

A. Hi-vol Filter Sample Methods

To compare results by the SulfaVer IV® method described in Appendix G with those by a previously evaluated procedure, extracts from samples collected on EPA Grade glass fiber filters were analyzed by this technique as well as the Colovos-MTB procedure[3], operated in the 0-80 µg/ml range. With both methods, analyses were done with three determinations obtained on separate days. The 24 filter samples employed were described in Section III. Extracts for intermethod comparison were prepared by pooling solutions remaining from the evaluation of extraction procedures.

The MTB method, is often employed without correction for the initial color of the sample.[18] Accordingly, samples were run without reagent to determine absorbance. Sulfate results were calculated both with and without correction by subtraction of initial sample absorbance.

The results, expressed as µg/ml of aqueous extract, are given in Table 18. The undiluted extracts covered a concentration range from ca. 30 to 230 µg/ml. With the SulfaVer IV® method, samples exceeding 55 µg/ml were diluted prior to analysis. For the MTB method, samples exceeding about 80 µg/ml were diluted prior to analysis.

The results are compared as ratios of means relative to corrected results by the Colovos-MTB method in Table 19. On average, the SulfaVer IV® method yielded results which were 10% higher.

Table 18

Results of Intermethod Comparison with Hi-Vol Filter Samples
(µg sulfate/ml)

Colovos-MTB[a]		SulfaVer IV[b]
Uncorrected	Corrected	
32.4 ± 0.4	29.7 ± 0.4	32 ± 1
42.1 ± 0.4	39.5 ± 0.4	45 ± 1
50.0 ± 0.4	45.9 ± 0.4	54 ± 1
55.7 ± 0.8	51.1 ± 0.8	55 ± 1
54.9 ± 0.5	51.5 ± 0.5	59 ± 1
55.0 ± 1	52.0 ± 1	59 ± 3
58.9 ± 0.5	55.0 ± 0.6	60 ± 1
61.6 ± 0.4	57.6 ± 0.5	80 ± 20
62.4 ± 0.3	58.2 ± 0.4	66 ± 2
62.9 ± 0.2	58.8 ± 0.1	64 ± 3
65.0 ± 1	60.0 ± 1	65 ± 6
66.5 ± 0.7	62.2 ± 0.6	69 ± 4
71.9 ± 0.4	66.6 ± 0.4	75 ± 3
73.5 ± 0.3	68.7 ± 0.6	78 ± 2
81.8 ± 0.9	76.2 ± 0.9	90 ± 2
91.8 ± 0.7	85.4 ± 0.7	94 ± 2
93.6 ± 0.3	87.6 ± 0.3	95 ± 5
99.2 ± 0.4	93.0 ± 0.5	102 ± 6
105 ± 1	98.8 ± 0.9	105 ± 1
116 ± 1	110 ± 1	123 ± 3
128 ± 1	122 ± 1	127 ± 4
142 ± 2	134 ± 2	146 ± 2
156 ± 2	150 ± 2	162 ± 9
230 ± 3	224 ± 3	230 ± 20

a. Samples diluted to < 80 µg/ml before analysis where necessary.

b. Samples above 55 µg/ml diluted to provide solutions below this concentration.

Table 19

Average Agreement and Precision of
Sulfate Methods with Hi-Vol Filter Samples

	Ratio of Means[a]	Median C.V. (%)	Range C.V. (%)
Colovos-MTB (corrected)	1.00	1.0	0.1 to 2.1
Colovos-MTB (uncorrected)	1.06	0.9	0.3 to 2.0
SulfaVer IV	1.10	3.2	1 to 20

a. Results expressed relative to those for the Colovos MTB method.

Correction of the MTB values for initial absorbance caused a decrease averaging 6%. Thus the uncorrected MTB and SulfaVer IV^{R} method differ, on average by 4%. These results may be compared to those previously found with slightly different versions of the SulfaVer IV^{R} and MTB methods[3]; in that case the SulfaVer IV^{R} results averaged 6% higher than those by Midwest Research Institute version of the MTB method.

The precisions of the methods are expressed by the median and range of the coefficients of variation. The 3.2% C.V. for the SulfaVer IV^{R} method compares to 5.3% found with the earlier version of this method. A more detailed comparison of the SulfaVer IV^{R} and Colovos-MTB (corrected) data is given in Figure 9. The results by the two methods are highly correlated. The substantial positive intercept leads to larger percentage differences for lower concentration samples.

B. Low-Volume Filter Sample Method

To compare the IC procedure for lo-vol filter samples to other procedures, extracts from the 24 samples collected in Los Angeles, described in Section IV, were analyzed by an MTB (0-10 µg/ml) method,* the AIHL microchemical method with ion exchange pretreatment[7] and by the IC. Analyses by the IC procedure were performed with three determinations on separate days. Because of the limited sample available, analyses by the other procedures were done with a single trial.

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*See page 19

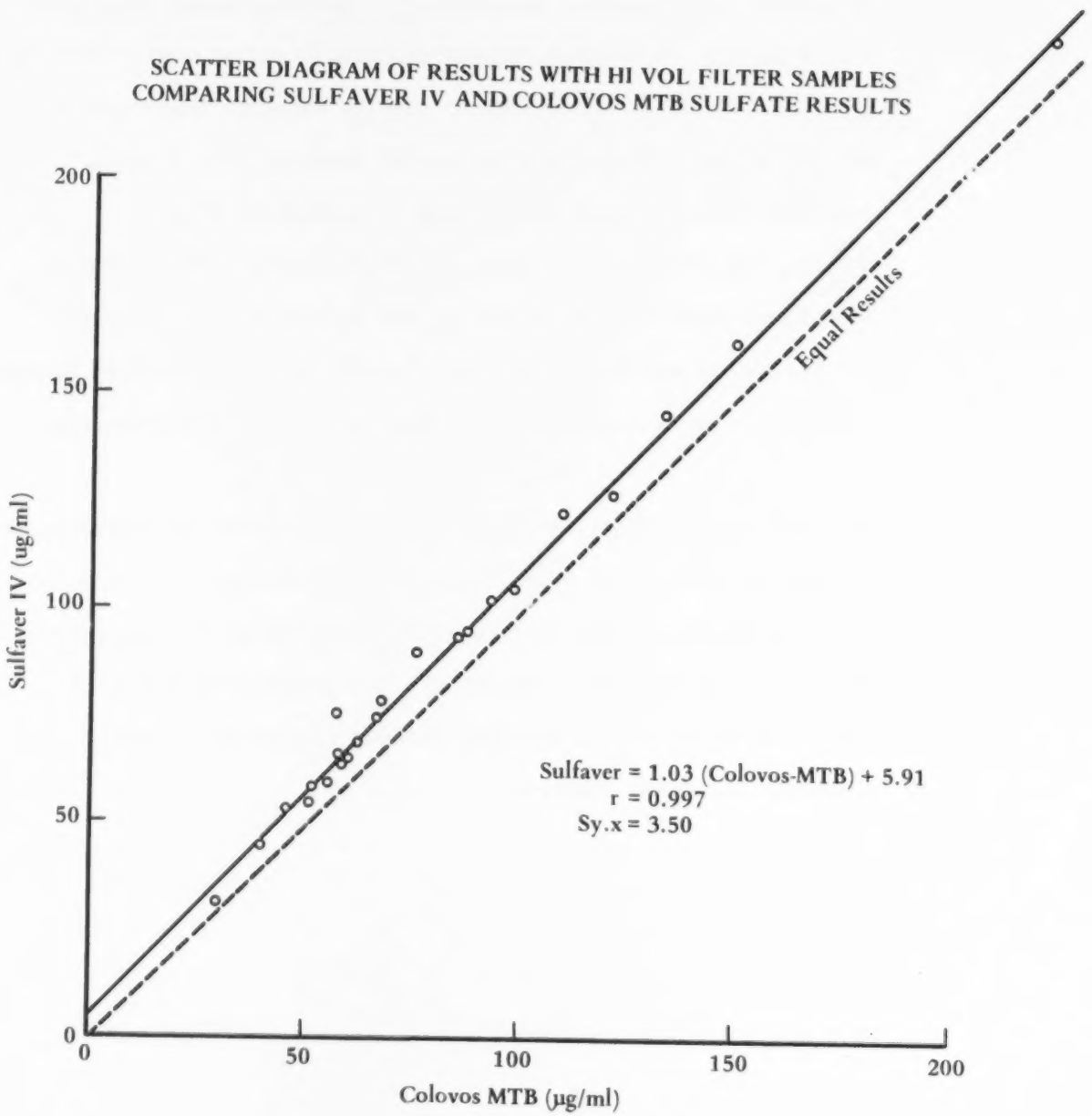

SCATTER DIAGRAM OF RESULTS WITH HI VOL FILTER SAMPLES
COMPARING SULFAVER IV AND COLOVOS MTB SULFATE RESULTS
Sulfaver IV (ug/ml)
Colovos MTB (µg/ml)
Equal Results
Sulfaver = 1.03 (Colovos-MTB) + 5.91
r = 0.997
Sy.x = 3.50
0
50
100
150
200

Figure 9

The results, expressed as µg/ml of aqueous extract, are given in Table 20 together with the ratio of means relative to the MTB procedure. The extracts covered a concentration range from about 1 to 9 µg/ml. On average, the three methods agreed within 6% with both the AIHL micro and Dionex IC results somewhat lower than by the MTB method. This trend for lo-vol samples by IC differs somewhat from that with hi-vol samples previously observed.[3] The latter study found, on average, IC results using a 30 µl sample loop to be about 4% higher than by two automated MTB procedures. Similarly, the earlier study found results by the AIHL micro method to be on average, about 2% higher than by the two MTB procedures.

The precision of the IC method with lo-vol samples, as expressed by the median coefficient of variation, was 6.5% (range 1.1 to 33.7%). A more detailed comparison of the methods is given in Figure 10. The results by the three methods are highly correlated with the lower results by the IC and AIHL methods persisting throughout the concentration range studied.

Table 20

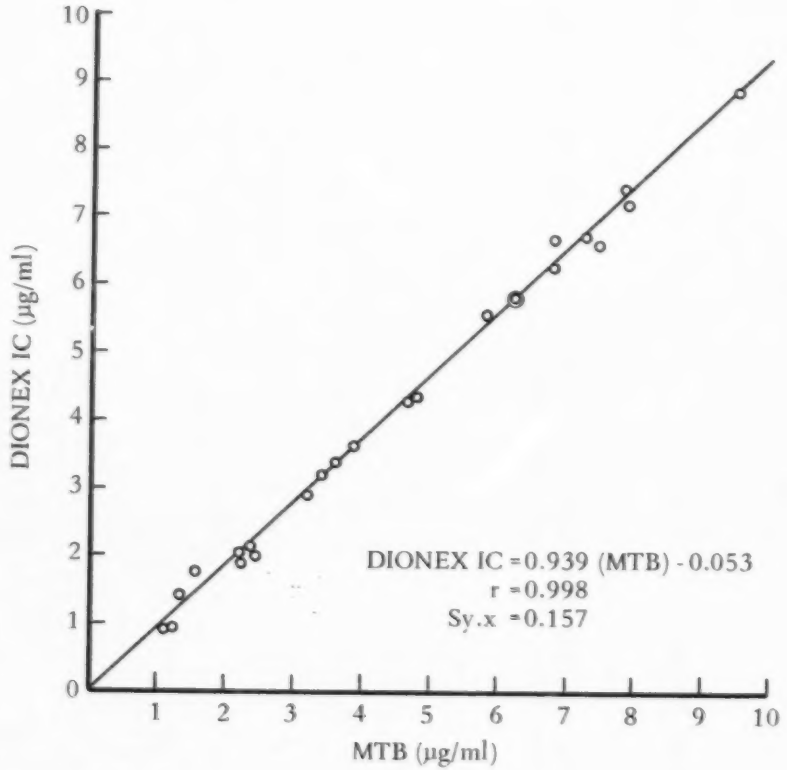
Results of Intermethod Comparison with Teflon Lo-Vol Filter Samples (μg sulfate/ml)[a]

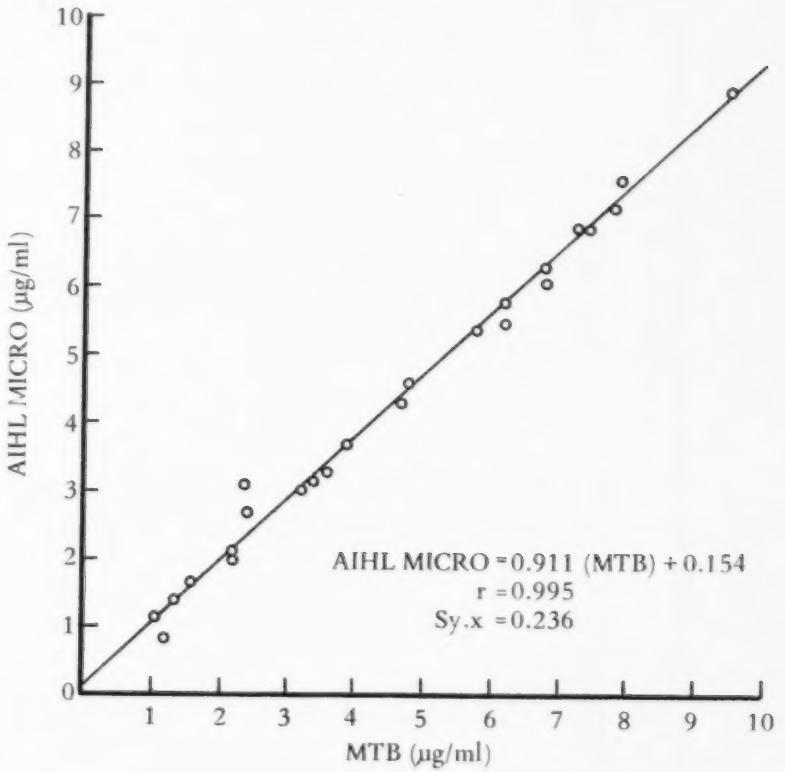
Sample ID	MTB	AIHL Micro	Dionex IC
L1D	1.20	0.88	0.92 ± 0.15
L4D	1.12	1.09	0.91 ± 0.19
L6C	1.35	1.41	1.38 ± 0.18
L3C	1.61	1.65	1.72 ± 0.58
L3D	2.18	1.98	2.02 ± 0.19
L2D	2.42	2.10	1.99 ± 0.18
L6D	2.22	2.15	1.93 ± 0.21
L5D	2.37	2.72	2.12 ± 0.11
L4A	3.20	3.05	2.92 ± 0.32
L1A	3.41	3.20	3.23 ± 0.39
L5A	3.60	3.29	3.36 ± 0.36
L2A	3.87	3.71	3.62 ± 0.34
L4B	4.70	4.35	4.34 ± 0.08
L1B	4.79	4.60	4.35 ± 0.06
L5C	5.82	5.43	5.56 ± 0.11
L3A	6.22	5.53	5.85 ± 0.45
L2C	6.20	5.77	5.87 ± 0.11
L1C	6.81	6.14	6.68 ± 0.21
L3B	6.78	6.32	6.31 ± 0.18
L2B	7.30	6.91	6.72 ± 0.16
L6B	7.44	6.94	6.59 ± 0.14
L6A	7.85	7.18	7.46 ± 0.37
L5B	7.93	7.61	7.20 ± 0.18
14C	9.51	8.92	8.88 ± 0.10
Ratio of Means:	1.00	0.944	0.928

a. All samples analyzed without dilution. Results for Dionex IC mean ± 1 σ for three determinations.

Figure 10

SCATTER DIAGRAMS OF RESULTS WITH LO VOL FILTER SAMPLES
USING THREE SULFATE METHODS





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APPENDIX A

Ultrasonic Extraction Procedure

The procedure used was taken from EPA-EMSL Method "Tentative Method for the Determination of Sulfates in the Atmosphere (Automated Technicon II Methylthymol Blue Procedure)":

> The filters are removed from the folder, opened flat, and cut into 1.9 by 20.3 (3/4 x 8 in.) strips using a pizza cutter. The filter should be cut with the particulates face up. One or more filter strips are placed in a 60-ml (2-oz) glass bottle. A random 5-10% of the filters should be extracted in duplicate for use as quality control samples. Fifty milliliters of distilled water are pipetted into each bottle. The bottles are then closed with polyseal caps. The samples are placed in the sonic bath, which should be refilled before each set of extractions with fresh cold tap water to the level of the liquid in the bottles. The sonic bath is operated for 30 min. The extracts are immediately vacuum filtered using the Buchner funnels and the vacuum filtering apparatus. The samples are filtered directly into polyethylene bottles. The filters should not be washed or squeezed, and the filtrates are not diluted. After filtering is complete, the polyethylene bottles are capped with polyseal caps and stored upright until analyzed. The samples are stable at room temperature for at least two weeks.

For the present study the above procedure was modified by employing 60 ml Erlenmeyer flasks with ground glass stoppers in place of 60 ml glass bottles. Filtration was done with a Millipore filtration apparatus using 0.7 μm cellulose ester filters, discarding the filter after each sample. During ultrasonic extraction 8 flasks were extracted simultaneously, distributed uniformly around the bath.

APPENDIX B

Reflux Procedure from AIHL Method 61*

One-fourth of the filter is cut into about 5-cm lengths for ease in handling and placed into the 125 ml boiling flask containing 50 ml of distilled water. The sample is refluxed for 60 minutes. The hot solution is filtered through a Whatman No. 42 filter paper which has been previously rinsed free of sulfate with at least 50 ml of boiling distilled water. The filtrate is collected in a 100 ml glass stoppered graduated cylinder. Both the boiling flask and sample filter are rinsed 3 times with about 10 ml each of boiling distilled water. After cooling, the final filtrate volume is brought up to 100 ml with distilled water.

*For the present study this procedure was modified by filtration as described in Appendix A.

APPENDIX C

Mechanical Shaking Procedure from BAAPCD Method S-4-2*

Cut up one quarter of the exposed glass filter into strips of about 3/4" by 1 1/2", place in 250 ml Erlenmayer flasks and add 50 ml distilled water. Seal the tops of the flasks with parafilm and shake the contents of the flask for one hour on the Burrel Shaker. Filter the samples thru dry filter paper into any suitable container for storage. Do not wash the residue or filter paper.

*For the present study this procedure was modified by filtration as described in Appendix A.

APPENDIX D

Sulfate Extraction from Teflon Filters by Mechanical Shaking

The filters were cut into quarters in a laminar flow clean bench and inserted into test tubes sealed with Teflon lined screw caps. Berkeley samples used 16 x 120 mm plastic tubes and Los Angeles samples, 16 x 150 mm glass tubes. To the Los Angeles samples was added 20 ml twice distilled H_2O and to the Berkeley samples, 10 ml.* The tubes were shaken in batches mounted horizontally on an Eberbach platform shaker at 90 oscillations/min for one hour. Sample filtration was performed using a Millipore vacuum filtration apparatus.

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*The dead volume in the tubes was approximately equal for the Berkeley and Los Angeles samples.

APPENDIX E

Sulfate Extraction from Teflon Filters by

Ultrasonic Extraction with Pre-wetting with Methanol

Uncut 37 or 47 mm filters were placed, unfolded, loaded side up in 100 ml plastic wide mouth containers. The Berkeley filters were wet by spotting with 0.2 ml anhydrous methanol, and the Los Angeles samples, with 0.4 ml. The filters were then weighted down with short sections of 3 mm glass rod bent into a "V", touching the filter at two points. To Los Angeles samples was added 20 ml twice distilled H_2O and to Berkeley samples, 10 ml. The apex of the glass rod extended above the liquid level. Filters were extracted for 30 minutes in batches of eight distributed uniformly within an ultrasonic bath. The liquid level in the bath was adjusted to be equal to that in the samples. Sample filtration was performed using a Millipore vacuum filtration apparatus.

APPENDIX F

Sulfate Extraction from Teflon Filters by Heating in Water at 80°C

Filters were cut in quarters and inserted into 16 x 150 mm Teflon lined, screw capped test tubes. To Los Angeles samples was added 20 ml twice distilled H_2O and to Berkeley samples, 10 ml. Samples were heated two hours at 80°C in thermostated heating blocks (Labline Inst. Co., #2090). Samples were then shaken briefly by hand and allowed to cool overnight. Sample filtration was performed using a Millipore vacuum filtration apparatus. No effort to weight down the filters was made. During heating filters are wet by condensing water vapor.

APPENDIX G

DETERMINATION OF SULFATE IN HIGH VOLUME PARTICULATE SAMPLES USING SULFAVER IV[R]*

Analyte:	Sulfate	Method No:	79
Application:	Air Pollution	Working Range:	180 to ≥ 1400 µg sulfate/20 ml
Matrix:	Air	Detection Limit:	Not determined
Procedure:	Collection on filter by high-volume sampler, extraction with water followed by turbidimetric analysis	Precision:	≤ 6% coefficient of variation in working range
		Accuracy:	Within 6%, on average, using EPA Audit Strips
Date First Issued:			

1. Principle of the Method

1.1 Atmospheric suspended particulate matter is collected over a 24-hour period on a 20 by 25-cm (8 by 10-inch) filter by using a high-volume sampler.

1.2 A water extract of the filter sample is treated with SulfaVer[R] from which barium chloride forms a barium sulfate colloidal suspension. The turbidity of the suspension is measured spectrophotometrically at 500 nm.

1.3 The extract is filtered through a Millipore filter to eliminate turbidity due to suspended particles or fibers.

1.4 Barium sulfate formation and turbidity measurements are done in test tubes (25 x 150 mm), thereby eliminating all sample transfers.

* The procedure was developed by E. M. Hoffer. Evaluation of the procedure is given in References 1 and 2.

Prepared by staff of the Air and Industrial Hygiene Laboratory Section, State Department of Health Services, Berkeley, California.

2. Interferences

2.1 Sample coloration and/or turbidity may interfere with the analysis. These interferences are minimized by filtration through a Millipore filter and by measuring the absorbance (A_1) of the filtrate before the addition of the SulfaVer IV®. This value is subtracted from the absorbance (A_2) of the sam le after the addition of SulfaVer IV®.

2.2 Sulfur-containing anions are generally strong positive interferents probably due to air oxidation to sulfate.[2]

2.3 Glass fiber filters contribute to observed sulfate both from a "blank" value and by artifact sulfate formation.[2,3] Artifact sulfate can be minimized by employing pH neutral filters (e.g. quartz fiber). With all filter types, the background or blank sulfate concentration should be measured (Section 7.3.4) for every lot and type of sampling filter used and the results corrected.

3. Precision and Accuracy

3.1 The precision of the method was established by three determinations on each of the extracts from 24 high-volume atmospheric samples ranging in concentration from 240 to 1500 µg sulfate per 20 ml solution. The median coefficient of variation was 5.3 (range 1.0 to 9.1%).

3.2 Accuracy was established by analyzing EPA audit strips (i.e filter strips loaded with known quantities of sulfate). For solutions in the range 300 to 1700 µg/20 ml, the ratio of observed to theoretical concentration ranged from 1.00 to 1.10 with mean value 1.06.

3.3 The extraction procedure, mechanical shaking in water at room temperature, was shown to extract, on average, 100% of the total water soluble sulfate in 24 high-volume filter samples.

4. Working Range

4.1 Working range is defined as the sulfate concentration range providing approximately constant coefficient of variation and "relative accuracy" The latter indicates the accuracy of the method relative to the value obtained in the optimal concentration range of the method. This is determined using a pooled, concentrated atmospheric sample extract, diluted to varying degrees.

4.2 This procedure yielded a relative accuracy within 4% in the concentration range 180 to 1400 µg sulfate/20 ml solution with a C.V. of $\leq$ 6%.

5. Equipment

5.1 High-volume Sampler. A motor blower-filtration system with a sampling head which can accommodate a 20 by 25-cm filter and capable of sampling at an initial flow rate of about 1.7 m^3/min (60 ft^3/min).

5.2 Filters. 20 by 25-cm (8 by 10-inch) filters.

5.3 Wrist Action Shaker. Burrell Model CC, Burrell Corp., Pittsburgh, PA

5.4 Filter Assembly

5.4.1 Funnel, 300 ml, Teflon faced, Millipore Catalog No. XX104724

5.4.2 Base, Teflon faced, Millipore Catalog No. XX104722

5.4.3 Spring clamp, anodized aluminum, Millipore Catalog No. XX104703

5.4.4 Stopper, Neoprene, No. 4 to fit Fisher Filtrator

5.5 Fisher Filtrator, low form (Catalog No. 9-788).

5.6 Millipore Filter. 47 mm plain white cellulose acetate, pore size in range 0.45 to 1.2 µm.

5.7 Filtrate Receivers. 60 or 100 ml polypropylene bottles with liquid tight caps.

5.8 Screw Capped Test Tubes. 25 x 150 mm, Teflon-lined. The tubes should be unscratched. Add a vertical fiduciary mark to permit reproducible positioning in the spectrophotometer.

5.9 Pipets. 5, 10, 20 ml and other sizes as required.

5.10 Spectrophotometer. Bausch and Lomb, Model 21 or equivalent.

5.11 Repipet. 10 ml capacity.

5.12 Platform Shaker. Eberbach Model 6000.

6. Reagents

6.1 SulfaVer IV^{R}Pillows. Catalog No. 12.065 obtainable from Hach Co., Loveland, Colorado 80537.

6.2 Standard Sulfate Solution (1000 µg sulfate/ml). Dry anhydrous sodium sulfate at 105°C for 4 hours and cool in a desiccator. Dissolve 1.479 g of the dried sodium sulfate in distilled water and dilute to 1 liter. This solution contains 1000 µg sulfate per ml.

7. Procedure

7.1 Sampling. Using the high-volume sampler, collect the particulate matter from approximately 2,000 m^3 of air. Twenty-four hours is the usual sampling period. Note and record the air flow rates at the start and end of the sampling period.

7.2 Sample Preparation. The sample filter should be delivered to the laboratory unfolded in a glassine envelope. Take an aliquot of the filter for analysis (Appendix 1 discusses sectioning the filter for various analyses). Cut one-fourth of the filter (Quadrant A as shown in Appendix 1) into strips about 1 to 1.5 cm wide for ease in handling. Place the strips into a 250 ml glass Erlenmeyer flask containing exactly 50 ml of distilled water, cover with

parafilm and shake for one hour on the Burrell shaker. Filter through an unused Millipore filter, (dull side up) using the Millipore filter assembly with a Fisher filtrator using vacuum (Figure 1). Place a 60 ml polyethylene container into the Fisher filtrator to receive the filtrate.

7.3 Analytical Procedure

7.3.1 Pipet aliquots of the filtrates, normally 20 ml, into a series of clean and dry screw-capped test tubes. When a smaller aliquot is used, dilute to 20 ml with distilled water.

7.3.2 Using the screw cap test tube as the spectrometer cell, with the fiduciary mark aiding reproducible positioning, determine the absorbance at 500 nm against distilled water.

7.3.3 The contents of one SulfaVer IV^{R} pillow are to be added to each of a batch of 12 samples in a test tube rack. To facilitate transfer, attach pillows to a jig in which the pillows are clipped at intervals corresponding to the intervals of the tubes in the test tube rack. Tap the pillows to settle contents to the bottom. Cut off pillow tops and carefully transfer contents, simultaneously, to a set of samples or standards contained in the test tubes. Tighten caps in each tube and mount batch of tubes horizontally in an Eberbach shaker set at 90 oscillations per minute. Shake 1 minute. After shaking, place the samples in a vertical position and wait 20 minutes at room temperature before reading absorbance (A_2). Read batch of 12 tubes

within 5 min. By spacing batches at about 5 minute intervals, determinations per day are maximized.

7.3.4 A correction for the concentration of sulfate in the filters must be made for each new lot of filters. This value (B) must be the average of at least 5 determinations using 5 filters from each lot of 100 filters using the entire analytical procedure and must be subtracted as filter blank (Section 9.2).

8. Standards and Calibration

8.1 Using the 1000 µg/ml sulfate standard prepare fresh weekly 100 ml of the following working standards:

µg $SO_4^=$/20 ml	ml of 1000 µg/ml standard
200	1.0
400	2.0
600	3.0
800	4.0
1000	5.0
1200	6.0
1400	7.0

Analyze 20 ml aliquots of these calibrating solutions together with each day's samples.

8.2 Plot the difference in absorbance readings (A_2-A_1) on the vertical axis versus the corresponding µg of sulfate on the horizontal axis using a rectilinear graph paper. The relation between absorbance and amount of sulfate should be approximately linear between 500 and 1400 µg/20 ml. By restricting samples to this range, linear

regression can be employed. For analyses in the range 180 to 1400 µg/20 ml, a third order regression equation is used of the form $y = a + bx + cx^2 + dx^3$ where x = µg/20 ml sulfate and y = absorbance.

9. Calculations

9.1 Air Volume Calculation

a. For samples collected at altitudes less than 2000 feet above mean sea level, use the calibrated air flow rate, which is approximately equal to the flow rate under standard conditions (760 Torr and 25°C).

b. For samples collected at altitudes of 2000 feet or greater, calibrate the high-volume sampler using the ARB procedure[4] which corrects the flow rate to standard sea level conditions.

c. Using the flow rate determined in (a) or (b) above, calculate the air volume from the sampling time and the average of the air flow rates at the start and end of the sampling period.

$$V = \frac{Q_1 + Q_2}{2} \times t$$

Where: Q_1 = air flow rate at start of sampling period (m^3/min) cubic feet per minute x 0.02832 = m^3/min.

Q_2 = air flow rate at end of sampling period (m^3/min) cubic feet per minute x 0.02832 = m^3/min.

t = sampling period (min).

V = sample volume in cubic meters (m^3) at standard conditions.

9.2 Subtract A_1 from A_2 and, calculating from the regression equation obtained in Section 8, determine the equivalent µg of sulfate (C) in the aliquot. Calculate the concentration of sulfate in the 20 by 25 cm filter sample, in $\mu g/m^3$ as follows:

$$\mu g \text{ sulfate}/m^3 = \frac{(F_1 \times F_2 \times C) - B}{V}$$

Where: $F_1 = \frac{\text{total ml of filtrate}}{\text{ml of filtrate taken for analysis}}$

$F_2 = \frac{\text{total sample area of filter sample}}{\text{sample area of filter quadrant analyzed}}$

C = µg sulfate in aliquot of sample taken

B = µg sulfate/20 x 25-cm filter blank

V = air sample volume in m^3 (determined as in Sec. 10.1)

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2. Final Report, EPA Contract No. EPA 68-02-1660, "Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate", B. R. Appel, E. L. Kothny, E. M. Hoffer and J. J. Wesolowski, February 1976.

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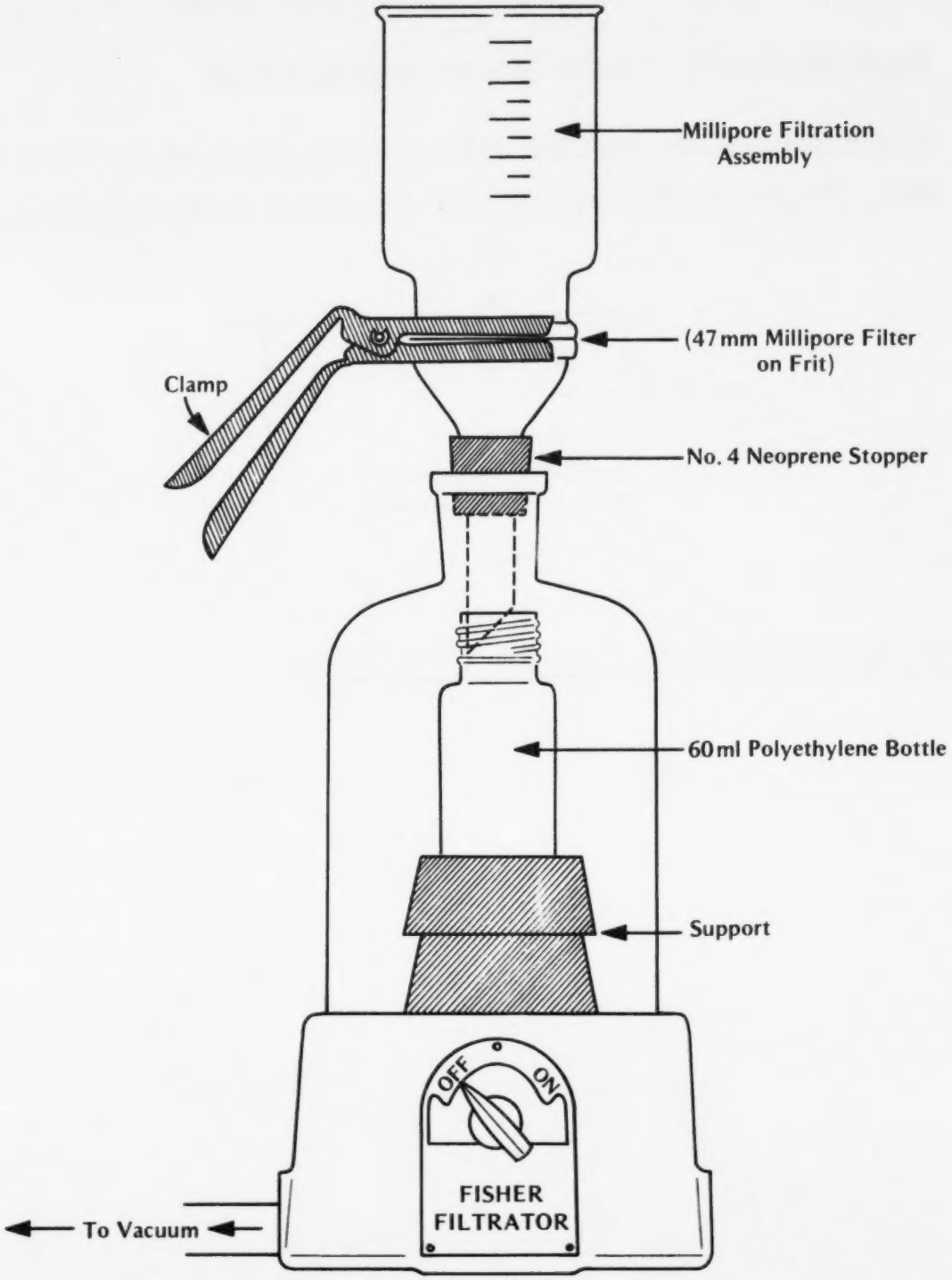
4. Standard Procedure for the Calibration of Hi-vol Samplers and Plotting of Flow Calibration Curves Corrected for Altitude, California Air Resources Board, September 1975, Sacramento, Calif.



Millipore Filter Assembly With Fisher Filtrator

Figure 1

Cutting of Glass-Fiber High-Volume Filters

1. Remove the glass-fiber filter from the shipping envelope.

2. Using a clean cutting tool, preferably stainless steel, cut the filter in half. Then cut one half into two equal quadrants as shown in Figure 1.

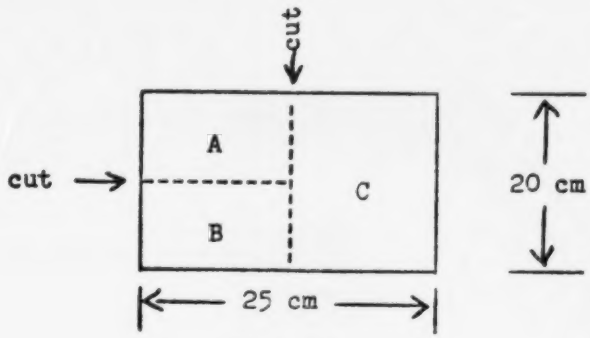


Figure 1

3. Use quadrant "A" for the determination of sulfate.

APPENDIX H

Ion Chromatographic Analysis of Sulfate in the Range 0 to 20 μg/ml

1. Equipment

1.1 Ion-Chromatograph. Dionex System 10 Ion Chromatograph, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94087.

1.2 Varian A-25 Recorder

1.3 Containers. 4oz. polypropylene containers with plastic screw-caps.

1.4 Filters (extraction). 0.45 μ disposable filter unit (Swinnex-25 Filter Unit, Millipore, or equivalent).

1.5 Syringes. 12 cc disposable syringes, without needle, graduations 0.2 cc. (Monoject Sterile Disposable Syringe, Cat. No. 512S, or equivalent).

2. Reagents

2.1 Water. The water for all reagents and suppressor column rinse should be distilled to a resistance of approximately 15 megohms, or conductivity of 0.1 to 1.0 micromho/cm or better. The water should be filtered free of particles larger than 0.20 μm unless a pre-column is used. Fill reservoir labelled "H_2O" in the chromatograph.*

2.2 Eluent. Prepare 0.003 M $NaHCO_3$-0.0024 M Na_2CO_3 solution as follows: In a 2-liter volumetric flask, dissolve 1.008 g $NaHCO_3$ (sodium bicarbonate, MCB, Cat. No. SX320 or equivalent) and 1.0175 g Na_2CO_3 (sodium carbonate, MCB, Cat. No. SX395-CB705 or equivalent) with distilled filtered water prepared as in 2.1 above. Invert gently to dissolve, make to the mark with deionized water, mix. Transfer to the eluent reservior Labelled "E_1" or "E_2" in the chromatograph.* Add an additional 2 liters water and mix well.

*When filling reserviors, avoid air bubbles which may cause pumps to lose their prime--see instruction manual for this procedure.

2.3 Regenerant. Prepare 1 N H_2SO_4 as follows: Into a 2 liter volumetric flask containing approximately 1 liter of distilled filtered water, introduce 111 ml of concentrated sulfuric acid, mix, cool. Make to the mark with deionized water, mix. Fill reservoir labelled "Regenerant" in the chromatograph. Add an additional 2 liters water to make a total of 4 liters, and mix well.

2.4 Stock Standard Sulfate Solution. (1000 µg sulfate/ml). Dry $(NH_4)_2SO_4$ (ammonium sulfate, NBS certified) powder at 105°C for 4 hours, cool in a desiccator. Dissolve 1.376 g of the dried ammonium sulfate in distilled water and dilute to 1 liter.

2.5 Stock Standard Nitrate Solution. (1000 µg nitrate/ml). Dry KNO_3 (potassium nitrate, NBS certified) powder at 105°C for 4 hours, cool in a desiccator. Dissolve 1.631 g of the dried potassium nitrate in distilled filtered water and dilute to 1 liter.

2.6 Sulfate Working Standards. Prepare working standards of 0, 2, 5, 10, 15, 20 µg/ml sulfate concentrations. To obtain the best accuracy and precision, weigh out the required amounts of stock standards into small beakers, and then transfer the contents to Class A volumetric flasks. Samples of higher concentration are set aside, diluted and analyzed at a later time.

Working Standard µg/ml Sulfate	ml or gms of Sulfate Stock Std. Added
0	0
2	0.20
5	0.50
10	1.00
15	1.50
20	2.00

After addition of stock standards to a 100 ml Class A volumetric flask, add sufficient double distilled water to the mark.

3. Analytical Procedure

3.1 Chromatograph Parameters

Range: 100 µmho

Recorder: 0.5 volts full scale, 10 inches/hour chart speed

Columns: 3 x 100 mm pre-column

3 x 250 mm anion separator column

6 x 250 mm anion suppressor column

Eluent: 0.0030 M $NaHCO_3$ + 0.0024 M Na_2CO_3

Elution Rate: 2.5 ml/min

Column and Detector Temperature: 35°C

Sample Loop: 0.5 ml

Under these conditions 20 µg/ml sulfate yielded a peak height of 80% of full scale.

3.2 Put the toggle switch on the front panel of the chromatograph in the LOAD position; using a syringe, inject 2 ml of sample solution into the injection port. Leave the syringe in place during chromatography.

3.3 Using the OFFSET COARSE or FINE knobs, adjust the indicator needle on the SPECIFIC CONDUCTANCE meter to 0.0.

3.4 Flip the toggle switch to the INJECT position, at the same time start the integrator or strip chart. After 15-30 seconds, flip the toggle switch back into the LOAD position.

3.5 Record the sample I.D. on the chart.

3.6 After the run is completed, rinse the sample loop with 3 ml of deionized filtered water with the toggle switch still in the LOAD position.

3.7 Inject the next sample as described in Sections 3.2 through 3.6.

4. Chromatograph Start-Up. (Review Ion-Chromatograph Instrument Manual)

4.1 Using the regulator on a dry air or nitrogen compressed gas cylinder, adjust the pressure to 90-100 psi for the air actuated valves in the chromatograph. Flip the toggle labelled AIR, on the front panel of the chromatograph, to the ON position.

4.2 Flip the toggle labelled POWER to the ON position.

4.3 Place the toggle labelled FLUSH down.

4.4 Place the toggle labelled $\frac{\text{INJECT}}{\text{LOAD}}$ down.

4.5 Place the toggle labelled $\frac{E_1}{\text{WATER}}$ up.

4.6 Place the toggle labelled E_2 up if E_1 is empty.

4.7 Place the toggle labelled E_2 down if reservoir E_1 is full.

4.8 Place the toggle labelled ANALYT up.

4.9 Place the toggle labelled SUPPRESS up.

4.10 Flip the toggle labelled PUMP to the ON position. Adjust the vernier dial on the front pump so that the flow rate is appropriate, e.g., 2.5 ml min. (The flow rate may be checked by disconnecting the output tubing from the suppressor column and placing the tubing in a graduated cylinder). Allow the system to run for 30 minute, or until the baseline drift is reasonably stable. Check for leaks in the tubing connections. Wear safety glasses when opening the column door. Check reservior levels.

4.11 Turn MODE switch to LIN.

4.12 Turn μMHO FULL SCALE to 100, initially, as in Section 3.1.

4.13 Set SPECIFIC CONDUCTANCE needle to 5.0 with the OFFSET COARSE and FINE knobs. (Allow sufficient positive baseline to account for any negative drift).

5. Standards and Calibration

5.1 Inject 3 ml of each of the standards described in paragraph 2.6. Record the reading by measuring the recorder trace (chromatogram) peak height.

5.2 Calculate linear regression lines for the standards from 5 to 20 µg/ml, based on the trailing peak height method. The response in this range is linear.

Calculate additional regression lines, for the standards from 0 to 5 µg/ml, as above. The Dionex response in this range is curvilinear and the results, therefore, less accurate using linear regression.

Alternately and preferably, set aside the samples below 5 µg/ml and rerun, using a more sensitive scale (e.g. 10 µmhos) and standards of 0, 1, 2, 3, 5 µg/ml.

5.3 To check for calibration drift over a day's run, rerun 5 and 20 µg/ml standards at 2 hour intervals. If the change in the regression slope is greater than 3%, calculate additional regression lines as needed, based on the new standards.

6. Regeneration of Suppressor Column

6.1 At the end of each day's run, the suppressor column may require regeneration as indicated by a color change in the column resin bed from tan to whitish tan, or by a swift rise in the conductance.

6.2 On the chromatograph, make the following settings:

6.2.1 Flip toggle switch labelled PUMPS to the OFF position.

Set the switch labelled MODE to ZERO.

6.2.2 Flip toggle switch labelled SUPPRESS to the down position.

Check the liquid levels in the regenerant and "H_2O" reservoirs.

6.2.3 Set TIME MIN indicators to 10 on REG side and 50 on RIN side.

6.2.4 Depress the green button labelled START, the rear pump should begin pumping. Set the vernier on the rear pump to approximately 90.

6.2.5 The cycle of regeneration is now automatic. At the end of the cycle, the pump will stop and the suppressor column will be tan colored. The cycle may be stopped prematurely by depressing the red colored button labelled RESET.

7. Chromatograph Shut Down

7.1 Flip the toggle switch labelled PUMP to the OFF position.

7.2 If the regeneration cycle is in process, and premature termination is necessary, depress the red button labelled RESET.

7.3 Flip toggle switch labelled POWER to the OFF position.

7.4 Flip AIR toggle switch to the OFF position.

7.5 Turn off regulator on compressed air or nitrogen cylinder.

7.6 Protect the integrator from dust using a plastic cover.

7.7 If the chromatograph is to be shut down for a long period of time (e.g., 2 months) rinse both columns with distilled water beforehand.